LEACHABILITY OF RADIUM-226 FROM BARIUM-RADIUM SULPHATE SLUDGES

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The National Uranium Tailings Program
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K1A 0G1

by

Dr. P. M. Huck
Department of Civil Engineering
University of Alberta
Edmonton, Alberta

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1.0 SUMMARY

The objective of this project was to examine the leachability of $^{226}Ra^{2+}$ from barium-radium sulfate sludges. The study included an elemental analysis of these sludges, geochemical modelling of the leaching of radium and microbiological experiments to investigate sludge solubilization.

Two sludges were investigated in the study. The first had been obtained in 1981 from the Rio Algom mine in Elliot Lake, Ontario. The second was obtained from the Cluff Lake mine in northern Saskatchewan in 1984.

Elemental analyses of the sludges showed the following range of composition for major elements: barium - 33-44%; sulfur - 14-22%; aluminum - 3-8%; calcium - 1-4%; and iron - 1-4%. In addition the following elements were found in concentrations ranging from 100 to 6,000 µg/g: strontium, potassium, magnesium, manganese, zinc, boron, copper and lead.

In the geochemical modelling task we undertook a literature review, the selection of an appropriate computer program to calculate equilibrium concentrations of the chemical species present, adaptation of the program to the University of Alberta's computer system, and a number of simulations.

The literature review indicated that the important geochemical factors affecting leaching were the sulfate and barium concentrations, the pH and ionic strength of the solution and the redox potential of the system. The leaching of radium from $(Ba,Ra)SO_4$ sludges is essentially controlled by the solubility of barium sulfate. Although no specific information on kinetic factors was found, it is likely that they would be very important.

Especially critical to assessing this solubility is understanding the characteristics of the related oxidizing and reducing (redox) systems that may be present. Shallow groundwater is typically an open or oxidizing system with a high redox potential. Such a system is dominated by dissolved oxygen.

Deeper groundwater where oxygen depletion has occurred is known as a closed or reducing system and is characterized by a low redox potential. Oxidizing agents in such systems are nitrate, manganese dioxide, ferric hydroxide and sulfate. Under reducing conditions primarily inorganic substances are reduced, the constituents oxidized are normally organic material. Most of these reactions are catalyzed by enyzmes or bacteria.

We prepared a simple computer code, designated SLUDGE, to simulate batch leaching under oxidizing conditions, i.e. where barium sulfate is a stable mineral phase and molecular oxygen is available. From an input consisting of sulfur and barium concentrations, pH and ionic strength, the program calculates the extent of barium sulfate dissolution and accompanying $^{226}Ra^{2+}$ release for an assumed specific activity of the barium sulfate.

We conducted the major modelling effort with a program denoted PHREEQE (PH REdox EQuilibrium Equations). This is a non-equilibrium reaction progress model developed by the U.S. Geological Survey to simulate geochemical reactions. As output this program produces pH and pe (electron activity) if these have not been previously specified, initial and final element concentrations and species distribution in solution, transfers to and from the aqueous phase (dissolution and precipitation) and the saturation state of the system with respect to specified minerals. We compared results from PHREEQE with those from SLUDGE. With PHREEQE we then simulated the effect of pH on leaching, a laboratory batch leaching experiment, the effect of various pe-pH conditions, the solubility or redox stability of barium sulfate in O_2-containing and O_2-free water, and the dissolution of barium sulfate in several hypothetical solutions.

We found agreement between PHREEQE and SLUDGE to be good and the PHREEQE model to be capable of reproducing in a general way previously-generated experimental leaching results. We prepared a stability diagram for the system Ba-S-O-H_2O. This Pourbaix diagram showed that conditions of pe and pH exist in nature in which $BaSO_{4(s)}$ is not a stable mineral phase. PHREEQE was able to reproduce the types of speciation found in this diagram.

Further simulations with PHREEQE showed that in O_2-containing water sufficient dissolution of barium sulfate would occur to produce saturation. In an O_2-free water, saturation is not reached because of sulfate reduction, and dissolution of barium sulfate would be at least a factor of 10^4 or 10^5 higher. Simulations involving hypothetical solutions undergoing pyrite oxidation showed that in the presence of gypsum only very limited dissolution of barium sulfate would occur.

From the geochemical modelling we concluded that the redox state of the system was the most important variable affecting sludge leaching. Since barium sulfate is not thermodynamically stable under reducing conditions all of the radium trapped in the precipitate could be released. While this would occur slowly because of unfavourable kinetics, very long times are of concern for sludge disposal. $(Ba,Ra)SO_4$ sludge is sparingly soluble under all oxidizing conditions, although radium release is enhanced at extreme pH values, high ionic strength and low barium or sulfur concentrations.

The second major aspect of the project consisted of experiments to determine the bacterial content of the sludges and the possibility of increased radium release through bacterial action.

We found that both the Elliot Lake and Cluff Lake sludges contained sulfate-reducing bacteria. The Cluff Lake sludge also contained sulfur-oxidizing bacteria. Since active heterotrophic bacterial populations existed in all samples, transformation of naturally-occurring organic matter into suitable substrates for the sulfate-reducing bacteria is possible.

We found that suitable carbon compounds could increase sulfate reduction in the sludges. Substantial releases of $^{226}Ra^{2+}$ occurred in these experiments. After an incubuation period of a number of weeks the $^{226}Ra^{2+}$ level in culture supernatants without lactate supplementation was 0.19-0.37 Ba/L. With lactate supplementation levels up to 425 Bq/L were measured. We found strong correlations between the barium, radium and sulfide levels in the supernatants, demonstrating that release of radium was due to dissolution of the sludge matrix. In a further experiment we found sulfate reduction to be rapid, with initiation occurring within five days. Thus bacteria act as catalysts to move a sludge-containing system much more quickly towards predicted equilibrium conditions.

From the microbiological experiments we concluded that substantial microbially-mediated radium release could occur under reducing conditions where suitable organic carbon was present and the pore water was low in sulfate. The sludges naturally contained suitable microbial populations for this activity.

In summary we have demonstrated that radium release from $(Ba,Ra)SO_4$ sludge is limited under oxidizing conditions. Under reducing conditions, however, barium sulfate is not thermodynamically stable and massive dissolution can eventually occur. We have shown experimentally that under suitable reducing conditions bacteria can produce substantial and rapid sludge dissolution with concomitant radium release. Disposal sites for barium-radium sulfate sludges should therefore be designed to maintain oxidizing conditions and to exclude organic matter.

2.0 INTRODUCTION

Canadian uranium mine-mill tailings decants are treated with barium chloride to remove $^{226}Ra^{2+}$. This has typically been accomplished in ponds which provide an opportunity for a barium-radium sulfate precipitate to form and subsequently settle. The treated effluent is discharged and the barium-radium sulfate sludge accumulates in the pond.

Upon mine closure, suitable final disposal locations for the accumulated sludge must be provided. Alternatives which have been suggested include placing the sludge in special chambers in worked-out mine areas or placing it back in the tailings area. Regardless of the disposal location, information must be available on the leachability of $^{226}Ra^{2+}$ from the sludge so that appropriate containment measures can be designed. In the case of disposal in tailings areas, of particular importance are the relative leachabilities of tailings and sludge and possible effects of sludge on release of radium from the tailings themselves. Although the amount of sludge is small in relation to the quantity of tailings, its specific activity is normally much higher.

Several recent studies have examined the leachability of $(Ba,Ra)SO_4$ sludge in the laboratory. However the information available on sludge leachability remains limited compared to the large amount of work which has been performed in defining radium releases from tailings. This study was designed to address significant information gaps which must be filled before sludge disposal strategies can be devised.

In recent years, powerful computer programs have become available to study complex geochemical processes involving multicomponent, multiphase equilibria in aqueous systems. These programs provide a quantitative means of simulating and interpreting a variety of laboratory and field-scale problems. It was one of our objectives to apply these geochemical modelling techniques to study the leaching of $^{226}Ra^{2+}$ from $(Ba,Ra)SO_4$ sludge.

Most of the previous sludge leaching studies examined only chemical aspects. Thus a second major objective of this investigation was to examine the role of bacteria in $(Ba,Ra)SO_4$ sludge leaching.

3.0 WORK STATEMENT

The initial scope of work for the study was comprised of the following tasks:

1. Geochemical modelling of sludge leaching,
2. Examination of fundamental sludge chemical characteristics,
3. Investigation of the role of bacteria in sludge leaching,
4. Lysimeter investigations of leaching,
5. Quality assurance, and
6. Submission of reports.

As the study evolved it became evident that the major investigative effort should be concentrated on Tasks 1 and 3. The contract was amended, and the scope of work then consisted of the following tasks:

1. Geochemical Modelling. This component of the study involved:
   (1) a literature review of the geochemical factors affecting the leachability of $^{226}Ra^{2+}$ from sludge,
   (2) the selection of the geochemical computer program best-suited for this study and the adaptation of it to the University of Alberta's computer facilities,
   (3) computer simulations to assess the importance of the factors identified in (1), and
   (4) computer simulations to evaluate the results of laboratory batch leaching experiments.

2. Chemical Analysis of Sludges. Detailed elemental analyses of an Ontario and a Saskatchewan sludge were completed.

3. Microbiological Experiments. These investigations determined the bacterial content of $(Ba,Ra)SO_4$ sludges, and examined factors affecting bacterial transformations of sludge by the indigenous flora which could result in the release of $^{226}Ra^{2+}$.

4. Quality Assurance. Standard samples provided by the Scientific Authority were analyzed for $^{226}Ra^{2+}$.

5. Reports. Quarterly progress reports were prepared. An interim report was submitted on July 15, 1984. An oral presentation was made to CANMET staff in Ottawa in July, 1985. The draft final report was submitted on July 31, 1985.

4.0 PREVIOUS INVESTIGATIONS

4.1 Geochemical Factors Affecting the Leaching of $^{226}Ra^{2+}$ from $(Ba,Ra)SO_4$ Sludges

The literature was reviewed to identify the geochemical factors influencing the leaching of $^{226}Ra^{2+}$ from $(Ba,Ra)SO_4$ sludges. The following characteristics of the leaching solution were found to be of major importance:

1. the sulfate (SO_4^{2-}) concentration
2. the barium (Ba^{2+}) concentration
3. pH
4. ionic strength
5. redox potential (pe or Eh)

The results of several studies indicated that competing ion effects and the liquid/solid ratio could also be important. The influence of temperature variations and the importance of kinetic factors were not investigated in detail in any of the papers reviewed. One factor identified as being unimportant was the liquid/solid contact time. A brief discussion of each factor is given in the remainder of this section.

It is well established that the amount of $^{226}Ra^{2+}$ leached from a $(Ba,Ra)SO_4$ sludge is controlled essentially by the solubility of $BaSO_{4(s)}$ in the leaching solution (1,2,3,4,5). The concentrations of Ba^{2+} and SO_4^{2-} in the leaching solution will therefore determine the amount of $(Ba,Ra)SO_4$ that will dissolve. If a solution in contact with the sludge is undersaturated with respect to $BaSO_{4(s)}$, dissolution of the $(Ba,Ra)SO_4$ component of the sludge will occur until thermodynamic equilibrium (i.e. saturation) has been established. The addition of either Ba^{2+} or SO_4^{2-} to a solution undersaturated with $BaSO_{4(s)}$ will decrease the degree of undersaturation. As a result less $(Ba,Ra)SO_4$ will dissolve, and correspondingly, less $^{226}Ra^{2+}$ will be released.

The pH of the solution is an important factor, although Gonzales, (1) found it to be unimportant in batch experiments over the range 2 to 10. However, the effect of extreme pH values on leachability has been demonstrated by others. Huck and Anderson, (6) investigated a range of pH values between 1.3 and 11.0. They obtained acidic pH's with HCl or H_2SO_4, and alkaline values with NaOH. Both low and high pH values increased radium leaching, with solutions of low pH being the strongest leachants. The mechanism(s) responsible for the augmented leaching was not specified. However, Huck and Anderson did allude to the possibility that a chemical reaction was responsible for the results observed at pH 1.3. At this pH, HSO_4^- rather than SO_4^{2-} is the dominant aqueous species, which forces the solution to become undersaturated with $BaSO_{4(s)}$.

The importance of ionic strength is not well-defined in the literature. In the discussion of their batch leaching results, McCready et al. (3) indicated that complex alterations of the sludge solubility may have been initiated by contaminating ions introduced to adjust the pH of the leachant. This statement suggests that the addition of pH-adjusting solutes or compounds caused a sufficient increase in the ionic strength of the solution to affect the solubility of the sludge. The increased solubility of $(Ba,Ra)SO_4$ in tailings caused by an increase in the ionic strength of the leachant was alluded to by Levins et al. (2). Theoretically, increasing the ionic strength would decrease the thermodynamic activity of Ba^{2+} and SO_4^{2-} resulting in an increase in leachant undersaturation. This would promote the dissolution of $(Ba,Ra)SO_4$ and the release of $^{226}Ra^{2+}$.

Huck et al. (7) mentioned that the oxidation potential of the leachant would be an important factor affecting radium leaching. No other information related to the redox potential (pe or Eh) of the leachant was found.

Very little information concerning the leaching of $^{226}Ra^{2+}$ at various temperatures was found. Huck et al. (7) noted that the solubility of $BaSO_{4(s)}$ doubles as the temperature increases from 0 to 20°C. In their experiments with tailings, Levins et al. (2) found that the extent of $^{226}Ra^{2+}$ leaching increased only slightly from 5° to 45°C.

Competing ion effects may be important in the leaching of $^{226}Ra^{2+}$ from $(Ba,Ra)SO_4$ sludge. The addition of cations to a leachant may create a high salinity condition which will increase the competition and exchange between ions in solution and those adsorbed on particle surfaces (7). This increased competition will increase the concentration of Ba^{2+} and $^{226}Ra^{2+}$ in solution. Levins et al. (2) observed that adding Na^+, Ca^{2+} and K^+ in large concentrations to a tailings leachant increased $^{226}Ra^{2+}$ leaching slightly, and that the addition of $BaCl_2$ significantly promoted leaching. They attributed this phenomenon to the increase in ionic strength and/or the displacement of adsorbed radium by the other cations. Anderson and Huck (8) observed that adding $BaCl_2$ in concentrations of 0.01 to 0.1 M to a solution caused significant amounts of radium to be leached from $(Ba,Ra)SO_4$ sludge. They also observed that the addition of NaCl, KCl, Na_2SO_4, $MgCl_2$ and $CaCl_2$ in concentrations ranging from 0.001 to 0.1 M failed to leach significant amounts of $^{226}Ra^{2+}$. These results indicate that decreasing the degree of undersaturation of the solution, and the associated decrease in $^{226}Ra^{2+}$ release due to the addition of Ba^{2+}, is less important than the displacement of adsorbed radium by Ba^{2+}.

The liquid/solid ratio used in batch leaching experiments should have an important effect on the amount of radium leached: as the volume of water increases, more mass must be dissolved to reach saturation. Levins et al. (2) in their work with tailings concluded that the liquid/solid ratio was the most significant factor, along with the SO_4^{2-} concentration, affecting radium leaching in uranium mill circuits. Huck et al. (7) also reported that increased liquid/solid ratios enhanced radium leaching from tailings, and Huck and Anderson (6) observed increased leaching from sludge with higher ratios.

Kinetic factors were not assessed in any of the reports reviewed. However, Powell et al. (9) indicated that the solubility of $(Ba,Ra)SO_4$ will be affected by structural irregularities in the crystals.

Constable and Snodgrass (5) demonstrated that $(Ba,Ra)SO_4$ is very insoluble. In their leaching experiments with tailings in high-rate lysimeters only 0.8% of the initial $^{226}Ra^{2+}$ in the $(Ba,Ra)SO_4$ was removed after 50 pore volumes had been passed through. In similar experiments with lysimeters packed with tailings and sludge less than 1% of the radium-226 was removed after seven years of leaching. These experiments would not however measure radium which might be leached and then readsorbed lower in the lysimeters.

4.1.1 Other Remarks

The following observations made by various researchers are important to consider in this study:

Sebesta et al. (4) have indicated that the equilibrium constant used in $BaSO_{4(s)}$ solubility calculations may have to be adjusted according to experimental conditions. Although the theoretical equilibrium constant has been established to be -9.98, Sebesta et al. have discovered from their field results that the actual value ranges from -8.95 to -9.23.

One characteristic of $(Ba,Ra)SO_4$ sludge noted in the literature was the presence of minor mineral phases. One Elliot Lake sample contained anhydrite ($CaSO_4$), portlandite ($Ca(OH)_2$), gibbsite ($Al(OH)_3$), goethite ($FeO(OH)$) and other unanalysed minerals in addition to $(Ba,Ra)SO_4$ (6, 10).

Constable and Snodgrass (5) made several important observations. Although radium coprecipitates only with $BaSO_{4(s)}$, it may be reversibly adsorbed onto various mineral phases. The important barium and radium species and compounds to be accounted for in sludge studies are reported to be Ba^{2+}, $BaSO_4°$, $BaSO_{4(s)}$, Ra^{2+} and $RaSO_4°$. The formation of $RaSO_{4(s)}$ will occur only if the molar ratio Ra^{2+}/Ba^{2+} is significantly greater than 10^{-6}. Radium forms $RaSO_4°$ complexes that are rapidly incorporated into a $BaSO_{4(s)}$ structure.

A bibliography on radium in uranium mine tailings and its removal by coprecipitation with barium sulfate was prepared as part of this study and is included as Appendix 1.

4.2 Redox-Controlling Factors in Hydrogeologic Systems

In the previous section it was noted that the redox state of a solution in contact with $(Ba,Ra)SO_4$ sludge will be a major factor governing the leaching of $^{226}Ra^{2+}$ from the sludge. It will be demonstrated later in this report that the sludge will be more stable in an oxidizing environment than in a reducing environment. In view of this, it is useful to provide a general overview of redox-controlling factors in hydrogeologic systems. Some of the information and equations presented below may be of use when designing computer simulation models in later studies of proposed disposal schemes. Much of the following was adapted from Freeze and Cherry (11) and the reader is referred to this textbook and others (12) for a more complete treatment of this topic.

4.2.1 General Characteristics

Surface waters exhibit oxidizing conditions because of their mixing with oxygen from the earth's atmosphere. When these waters enter a groundwater flow system and move along flow paths to greater depths, oxygen depletion generally occurs and reducing conditions may be produced. This happens because the oxygen consumed by chemical and biochemical reactions is not replenished. An open (or oxidizing) system usually exists in the very shallow parts of groundwater flow systems and is characterized by the presence of measurable amounts of dissolved oxygen. In the deeper parts of the flow systems where dissolved oxygen has been essentially depleted, the redox condition is referred to as being closed or reducing. The boundary between open and closed systems depends on soil conditions. For example, in recharge areas with coarse-grained soils, the shallow groundwater commonly contains detectable levels of dissolved oxygen (ie. > 0.1 mg/L) and, therefore, open conditions exist. Closed-system conditions occur in recharge areas with silty and clayey soils. Dissolved oxygen at detectable levels commonly persists far into the flow system in areas with little or no soil overlying permeable fractured rocks.

The oxidation and reduction of inorganic constituents is a major geochemical process occurring in the subsurface. Only a few elements, i.e. carbon, nitrogen, oxygen, sulfur, iron and manganese, are predominant participants in these redox reactions. Many of the important redox reactions involve the reduction of inorganic constituents; the most common oxidized material in these reactions is organic matter. Almost all of the reactions are catalyzed by isolated enzymes, or by bacteria that derive energy by facilitating electron transfer. These organisms do not perform the actual redox process, but only mediate the reaction.

4.2.2 Redox Characteristics of Open Systems

The oxidation-reduction state of a system is expressed as the redox potential, measured in units of Eh, or the electron activity, expressed as pe. High redox potentials or electron activities indicate oxidizing conditions; low (negative) values indicate reducing conditions. Precipitation entering the soil zone has a high redox potential from exposure to atmospheric oxygen and exhibits pe values in the range of 12 to 14. Within this range all other elements should exist almost completely in their highest naturally-occurring oxidation states. For example, carbon will exist as CO_2, HCO_3^- or CO_3^{2-}, nitrogen as NO_3^-, sulfur as SO_4^{2-}, iron as FeO(OH) or Fe_2O_3 and manganese as MnO_2. As the precipitation infiltrates the soil zone the redox potential drops due to the oxidation of organic matter and inorganic consitutents, causing the removal (reduction) of most of the dissolved oxygen.

The oxidation of organic matter is the dominant reaction consuming dissolved oxygen. This reaction is expressed as:

$$CH_2O + O_{2(g)} = CO_{2(g)} + H_2O$$

where "CH_2O" represents organic matter. This reaction is also the main source of $CO_{2(g)}$ in the soil zone. The $CO_{2(g)}$ produced will react with H_2O to generate H_2CO_3, decreasing the pH of the solution. Dissolution of minerals such as calcite, dolomite, gypsum and anhydrite will occur in the presence of H_2CO_3.

The oxidation of inorganic consitutents will also consume oxygen. Five of the more common reactions are:

$$2O_2 + HS^- = SO_4^{2-} + H^+ \qquad \text{(sulfide oxidation)}$$

$O_2 + 4Fe^{2+} + 4H^+ = 4Fe^{3+} + 2H_2O$ (iron oxidation)

$2O_2 + NH_4^+ = NO_3^- + 2H^+ + H_2O$ (nitrification)

$O_2 + 2Mn^{2+} + 2H_2O = 2MnO_{2\,(s)} + 4H^+$ (manganese oxidation)

$\frac{15}{4}O_2 + FeS_{2(s)} + \frac{7}{2}H_2O = Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+$ (iron sulfide oxidation)

All of the above reactions are characterized by the production of acid (H^+).

4.2.3 Redox Characteristics of Closed Systems

The solubility of oxygen in water is low (9 mg/L at 25°C) and its rate of replenishment in subsurface environments is very low. As a result, the oxidation of only a small quantity of organic matter or inorganic compounds can consume all the dissolved oxygen. The oxidation of organic matter will still occur but the oxidizing agents (constituents that will be reduced) are compounds such as NO_3^-, MnO_2, $Fe(OH)_3$ and SO_4^{2-}. As these oxidizing agents are consumed, the groundwater environment becomes more and more reduced. Examples of redox reactions that oxidize organic matter and reduce inorganic compounds are:

$CH_2O + \frac{4}{5}NO_3^- = \frac{2}{3}N_{2(g)} + HCO_3^- + \frac{1}{5}H^+ + \frac{2}{5}H_2O$ (denitrification)

$CH_2O + 2MnO_2(s) + 3H^+ = 2Mn^{2+} + HCO_3^- + 2H_2O$ (manganese IV reduction)

$CH_2O + 4Fe(OH)_{3(s)} + 7H^+ = 4Fe^{2+} + HCO_3^- + 10H_2O$ (iron III reduction)

$CH_2O + \frac{1}{2}SO_4^{2-} = \frac{1}{2}HS^- + HCO_3^- + \frac{1}{2}H^+$ (sulfate reduction)

$CH_2O + \frac{1}{2}H_2O = \frac{1}{2}CH_4 + \frac{1}{2}HCO_3^- + \frac{1}{2}H^+$ (methane fermentation)

The sequence of the above redox reactions proceeds from aerobic oxidation through to methane fermentation provided that:

1. organic matter in a consumable form continues to be available in the water,

2. the bacteria that mediate the reactions have sufficient nutrients to sustain their existence,
3. the temperature variations are not large enough to disrupt the biochemical processes.

In many groundwater systems one or more of these factors is limiting, so the groundwater does not proceed through all of the redox stages.

4.3 Microbiological Aspects of Radioactive Waste Disposal

There are only a few reported studies on microbial activity associated with the disposal of radioactive waste materials. Ausmus *et al*. (13) have recommended that the activities of microbes be considered in burial grounds for low-level wastes. Metabolic activities of these organisms can transform stable radioactive wastes into mobile compounds and can hasten the deterioration of containers used in the disposal of these materials.

Francis *et al*. (14,15) have studied the microbial activity of trench leachates from disposal sites which received low-level radioactive wastes including ^{3}H, ^{14}C, ^{60}Co, ^{90}Sr, $^{134,137}Cs$, ^{241}Am and $^{238,239,240}Pu$. Aerobic and anaerobic bacteria, sulfate-reducing, denitrifying and methane bacteria were detected in leachate samples. Many organic compounds were identified in the leachate (16) and some of these were biodegraded under anaerobic conditions (15). Radioactive methane ($^{14}CH_4$ and $^{3}HCH_3$) was also produced by microbial activity in the leachate (14).

The majority of the microbiological studies pertaining to uranium mining have dealt with recovery of uranium from low grade ores. Typically, *Thiobacillus ferrooxidans* has been used to form soluble uranyl ions (UO_2^{2+}) which can be leached from the ore (17, 18). However, Silver and Ritcey (19) have studied the effects of sulfur-oxidizing bacteria on the release of $^{226}Ra^{2+}$ from uranium mine mill wastes which contained 0.72% pyrite. Their study compared the effluent characteristics from lysimeters which had been inoculated with sulfur-oxidizing bacteria with that of a lysimeter which was treated with hypochlorite to reduce microbial activity. The results from their work showed that the bacterial oxidation of the sulfide minerals increased the amount of sulfate and decreased the amount of $^{226}Ra^{2+}$ in the effluent.

Bolze *et al.* (20) have shown that $BaSO_4$ can be dissolved by microbial action under anaerobic conditions. Gilkeson *et al.* (21) attributed high Ba^{2+} concentrations in aquifers to the bacterially mediated reduction of sulfate in anaerobic zones of the aquifer. McCready and Krouse (22) have demonstrated that *Desulfovibrio vulgaris* was able to use a $BaSO_4$ precipitate as a sulfur source. They postulated that the rate of dissolution of $BaSO_4$ (which has a solubility in water at 25°C of 2.4 mg/L) limited the rate of microbial sulfate reduction. McCready *et al.* (3) prepared a $(Ba,Ra)SO_4$ sludge and showed that *D. vulgaris* can release H_2S, $^{226}Ra^{2+}$ and Ba^{2+} from the precipitate.

5.0 ANALYSIS OF NUTP RADIUM STANDARDS

At the request of the Scientific Authority we participated in a $^{226}Ra^{2+}$ standards program to establish our analytical capability for this parameter. All standards were provided by CANMET. All $^{226}Ra^{2+}$ analyses were performed using the radon de-enamation method which is described in detail in Appendix 2.1.

The first standard analyzed was aqueous and was designated as Standard A. The $^{226}Ra^{2+}$ activity level of the standard was determined to be 2.41 ± 0.37 Bq/L (Table 1). The NUTP reported that the standard was made up to be 1.85 ± 0.19 Bq/L.

The second standard anlayzed was supplied as a $(Ba,Ra)SO_4$ precipitate. This solid was dried, weighed and dissolved as described in Appendix 2.1. The $^{226}Ra^{2+}$ activity level of the standard was determined to be 7.40 ± 1.0 Bq/g (Table 2). The NUTP reported that the standard was made up to be 2.96 Bq/g. Because of this large difference the Saskatchewan Research Council (SRC) was engaged to confirm the value of the Standard. They reported the activity of the standard to be 3.74 Bq/g (Appendix 2.1).

The SRC result indicated that there was a problem with our $^{226}Ra^{2+}$ analytical capability. With assistance provided by the SRC, modifications were made to the degassing procedure to improve the accuracy of our method.

Following these modifications a new $^{226}Ra^{2+}$ standard was obtained from the National Bureau of Standards (NBS) in Gaithersburg, MD, U.S.A. (Appendix 2.1). The counting efficiency of our three radon detectors was then re-determined and a new cell calibration constant established for each. Five new standards were then obtained from the NUTP and analyzed for $^{226}Ra^{2+}$.

Table 1. $^{226}\text{Ra}^{2+}$ Activity Level Determination - NUTP Standard A (Aqueous)

Split Sample*	Sample 1**	Sample 2	Sample 3
	2.44	2.41	2.22
	1.74	2.22	2.33
	2.04	1.92	2.92
	2.78	2.29	3.00
	2.81	2.66	-
Mean	2.37	2.30	2.63
Standard deviation	0.48	0.30	0.41
Co-efficient of variation	19%	13%	15%
Overall mean		2.41	
Overall standard deviation		0.37	
Overall co-efficient of variation		15%	
Activity level of standard (as reported by NUTP)		1.85 ± 0.19	
$\frac{\text{U of A activity level}}{\text{NUTP activity level}} \times 100\%$		130%	

* Standard A split into three 130 mL samples.
** All $^{226}\text{Ra}^{2+}$ activity levels reported in Bq/L.

Table 2. $^{226}\text{Ra}^{2+}$ Activity Level Determination - NUTP Standard B [$(\text{Ba,Ra})\text{SO}_4$ Solid]

	Sample 1*	Sample 2	Sample 3	Sample 4
	7.96	7.66	8.07	8.18
	7.22	7.62	8.21	8.29
	8.10	6.48	8.55	7.36
	8.33	6.22	9.14	7.73
	7.51	5.11	7.25	6.66
	8.21	5.74	-	-
	6.77	7.07	-	-
	7.73	5.18	-	-
Mean	7.73	6.38	8.25	7.64
Standard deviation	0.52	1.00	0.70	0.67
Co-efficient of variation	7%	16%	9%	9%
Overall mean			7.50	
Overall standard deviation			1.04	
Overall co-efficient of variation			14%	
Activity level of standard				
- as reported by NUTP			2.96	
- as determined by SRC			3.70	
$\frac{\text{U of A activity level}}{\text{NUTP activity level}} \times 100\%$			253%	

* All $^{226}\text{Ra}^{2+}$ activity levels reported in Bq/g.

Samples 1 through 4 were aqueous and were analyzed directly. Sample number 5 was supplied as a (Ba,Ra)SO_4 precipitate. This solid was desiccated overnight and then 1.09047 g was dissolved at 88°C with stirring in 1.0 L of 0.1 N EDTA (disodium salt) adjusted to pH 11.0 with NaOH. Following cooling overnight 130 mL of this solution was transferred to each of two bubbler tubes. This volume represented 0.141761 g of solid assuming that all the precipitate dissolved, as appeared to be the case.

The results of these determinations (Tables 3 and 4) were much closer to the values reported by the NUTP. The Scientific Authority advised that our $^{226}Ra^{2+}$ analytical capability was satisfactory for completion of the study.

Table 3. $^{226}\text{Ra}^{2+}$ Activity Level Determinations - NUTP Standards 1 Through 3 (Aqueous)

	Sample 1*	Sample 2	Sample 3
	1.41	3.37	10.32
	1.41	3.48	11.32
	1.59	3.40	9.44
	1.44	4.81	10.14
	1.85	3.89	12.69
	1.48	4.48	14.50
Mean	1.53	3.91	11.40
Standard deviation	0.16	0.63	1.89
Co-efficient of variation	10%	16%	17%
Activity level of standard (as reported by NUTP)	1.67 ± 0.44	4.63 ± 0.93	11.84 ± 0.26
$\frac{\text{U of A activity level}}{\text{NUTP activity level}} \times 100\%$	92%	84%	96%

* $^{226}\text{Ra}^{2+}$ activity levels reported in Bq/L.

Table 4. $^{226}\mathrm{Ra}^{2+}$ Activity Level Determinations - NUTP Standards 4 and 5

Split Sample	Sample No. 4 (aqueous)			Sample No. 5 (solid)	
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2
	13.06	11.29	9.92	2.74	3.03
	12.58	12.14	11.66	2.96	2.81
	9.95	10.51	9.21	2.96	2.92
	10.58	12.17	13.58	2.29	3.11
	10.73	13.14	9.99	2.74	2.63
	9.95	10.58	12.06	-	-
	11.80	12.99	12.65	-	-
Mean	11.24	11.83	11.30	2.74	2.90
Standard deviation	1.26	1.07	1.63	0.26	0.19
Co-efficient of variation	11%	9%	14%	9%	7%
Overall mean		11.46		2.82	
Overall standard deviation		1.30		0.22	
Overall co-efficient of variation		11%		8%	
Activity level of standard (as reported by the NUTP)		11.84 Bq/L		2.37 Bq/g	
$\frac{\text{U of A activity level}}{\text{NUTP activity level}}$ x 100%		97%		119%	

*Units for sample number 4 are Bq/L, sample number 5 is expressed in Bq/g. Sample no. 5 was labelled $(Ba,Ra)SO_4$ standard no. 1 by CANMET.

6.0 SLUDGE ELEMENTAL ANALYSIS

6.1 Sources of $(Ba,Ra)SO_4$ Sludges

In this project sludges from two Canadian uranium mines were analyzed. One sludge sample had been collected in October, 1981 by dredging sediment from Pond 1 of a lined two-pond treatment pilot plant in Elliot Lake, Ontario. The pilot plant treated decant from Rio Algom's Quirke tailings basin. These tailings are from a sulfuric acid leach mill and are limed prior to discharge from the mill. Treatment at the pilot plant basically involved the addition of 15-30 mg/L $BaCl_2$ to the tailings basin overflow (23). These samples had been stored at room temperature (approximately 20°C) for approximately three years prior to the beginning of this study.

Amok's Cluff Lake mining site in Saskatchewan was the second source of samples. In May 1984, samples from four locations (Figure 1) were collected in sterile 500 mL polyethylene bottles. Sludge and overlying water were collected from the tailings pond, the A-2 treatment pond and the B-1 treatment pond. Sediment from the nearby Snake Lake was collected as a control sample for microbiological analyses. These samples were stored at 4°C prior to their examination.

Between May 25 and June 29, 1984, a sample of $(Ba,Ra)SO_4$ sludge was collected from the first (A-1) settling pond following $BaCl_2$ addition at the Cluff Lake site. The sludge was obtained by placing two weighted polyethylene traps on the plastic liner surface of the pond in approximately 1.5-2.0 m of water. The traps were fixed to the shore with polypropylene cords and were removed once every two weeks to remove settled sludge. The sludge was then poured into a 25 L polyethylene container; following settling excess liquid

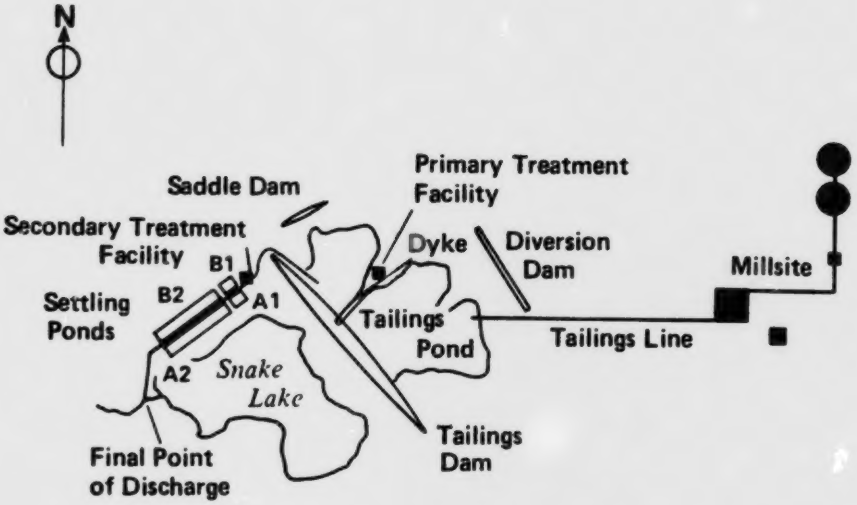

N
Saddle Dam
Primary Treatment Facility
Secondary Treatment Facility
B1
Dyke
Diversion Dam
Millsite
Settling Ponds
B2
A1
Tailings Pond
Tailings Line
A2
Snake Lake
Final Point of Discharge
Tailings Dam

Figure 1. General Arrangement of the Effluent Treatment System at Cluff Lake, Saskatchewan (24)

was decanted.

Upon arrival in the laboratory, the contents of the 25 L container were vigorously agitated and aliquots were aseptically transferred into sterile 1 L bottles. These were stored at 4°C for one week prior to microbiological examination.

6.2 Sludge Handling and Dissolution Procedures

To obtain subsamples of each sludge for analysis, two sample bottles from each mine were chosen. For each bottle, approximately two grams of wet sludge was filtered through Whatman #2 filter paper. Approximately 0.5 g portions of the wet sludge were then transferred to preweighed vials. The vials plus contents were reweighed and placed in a 110°C oven until constant weight was achieved.

For each bottle, three of the dried samples were selected for dissolution and analysis. The method of naming each subsample is described in Figure 2. The complete dissolution procedure is described in Appendix 2.2.

Figure 2. Sludge Subsample Nomenclature

1. Rio Algom Ltd - Elliot Lake Sludge

RA XYY-Z

RA - Sample origin (Rio Algom)
X - Jerry can number
YY - Bottle number
Z - Subsample number

2. Amok Ltd - Cluff Lake Sludge

CL YY-Z

CL - Sample origin (Cluff Lake)
YY - Bottle number
Z - Subsample number

Also: A1 which is pond A1 from the secondary treatment system (STS) and A2 from the same system. All 'CL' samples were taken from pond A1.

Note: Samples designated A1 and A2 were obtained shortly before this study began while settling ponds were being 'cleaned out'. Increased sludge volume caused by heavy dosing of the tailings decant with lime ($Ca(OH)_2$) in the winter of 1984 necessitated the removal of sludge from these ponds.

The Cluff Lake samples changed colour while drying. The wet sludge samples were black, indicating the presence of sulfides, and smelled of hydrogen sulfide. After drying, the samples were light brown. No attempt was made to measure the quantity of H_2S lost from the samples during drying.

For the dissolution procedure all samples were digested in 0.05 M EDTA adjusted to pH 10.5 with NaOH on a hot plate at 90°C for 12 hours.

Following digestion, two different forms of solid material remained. At the high pH of the solutions any iron present is precipitated as hydrous iron oxide. The characteristic red precipitate of this oxide was especially apparent in the Rio Algom sludge. In addition to the red iron precipitate, solid particles visually similar to sand grains were observed. Corrections to analyses were made to account for the undissolved material, as described in Appendix 2.2.

Table 5 shows the average solids content and amount of undissolved matter for each sample. The undissolved material ranged between 7.6 and 9.8% for the Rio Algom sludge and between 2.0 and 4.1% for the Cluff Lake sludge. It is interesting to note that the residue in the lime-treated samples (A1 and A2) was approximately 2% while in the untreated samples from Cluff Lake it was almost double that amount, or about 4%.

6.3 $^{226}Ra^{2+}$ Analyses

All sludge samples were dissolved using the procedure described in Appendix 2.2. Because of the anticipated high activity level of the samples only 10 mL was removed from each. This volume was then made up to 130 mL with high purity deionized water and analyzed as described in Appendix 2.1. Results from these analyses are reported in Table 7.

Table 5. Solids Content and Undissolved Matter for Sludge Samples

Sample*	Average Percent Solids (Dry Weight Basis)	Percent Undissolved Matter After Dissolution
RA 12	45.72	8.6
RA 114	42.23	9.0
CL 6	37.64	3.5
CL 18	24.60	4.0
A1	25.88	2.2
A2	15.73	2.0

* All mean determinations are based on three values with the exception of CL 6 which is based on two samples (see Tables 2.2-1 and 2.2-2 in Appendix 2).

6.4 Inductively Coupled Plasma (ICP) Method

In determining the elemental composition of the sludge samples, emphasis was placed on measurement of the metal content. For this reason inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was chosen as the analytical method. A complete description of the method is provided in Appendix 2.3. Only a brief summary is given here.

To compensate for the presence of matrix effects in the sludge samples, the technique of standard addition was used. In this technique a known quantity of the analyte element is added to the unknown solution. In the present study, only major elements were determined using the standard addition technique. These elements were barium, sulfur, calcium, iron, aluminum, magnesium, manganese, and zinc.

A preliminary analysis required to determine the conditions for the standard addition was performed by Sherritt-Gordon Mines Ltd., Fort Saskatchewan, Alberta. The results are listed in Appendix 2.3. On the basis of these results standard-addition concentrations were calculated and prepared for the final analyses.

6.5 Results

6.5.1 Supernatant Solutions

The results of the analysis of supernatant samples from the RA 12, RA 114, CL 6 and CL 18 bottles are summarized in Table 6. Elements not present at concentrations above the detection limit were: Zr, Ni, Sn, Cr, Sb, Ge, Cu, Pb, Ti, Cd and In. As expected, the barium concentrations are low, approximately 0.03 mg/L for the Rio Algom and 0.5 mg/L for the Cluff Lake supernatant solutions. Sulfur, likely present as excess sulfate, follows the reverse trend in concentration. In the Rio Algom supernatant solutions the sulfur concentration is in the range of 425 mg/L while in those from Cluff Lake it is lower, approximately 250 mg/L. Major differences between the two localities include the high concentrations of manganese, magnesium and sodium in the Cluff Lake supernatant relative to Rio Algom. Also, trace levels of aluminum, arsenic and vanadium were found in the Cluff Lake solutions, but none of the three were detected in those from Rio Algom.

The uncertainty reported for each value in Table 6 is that of the measurement step and is the relative standard deviation of the three individual measurements.

6.5.2 Sludge Samples

The detailed analyses of individual sludge subsamples is presented in Appendix 2.3, along with a discussion of the uncertainty of the measurements. The average results for each sample are summarized in Table 7.

Only those elements present at concentrations above the detection limits given in Appendix 2.3 are listed in Table 7. Those elements not present at detectable concentrations are: Zr, Ni, Hg, As, Sn, Mo, Sb, Ge, Ag, Li, Ti, Cd and In.

There are several marked differences between the Cluff Lake and Rio Algom sludge samples. One example is sulfur content: the Cluff Lake sludge has a sulfur concentration of more than 20%, compared to only approximately 15% found in Rio Algom sludge. The presence of sulfide was apparent visually in the Cluff Lake sludge samples. Although some H_2S was likely lost in the drying process, a higher sulfide content and therefore a higher sulfur concentration might be expected as compared to the Rio Algom samples. Estimation of sulfide to sulfate ratios is not feasible in these measurements since the ICP is only capable of measuring elemental composition.

Table 6. Analysis of Supernatant from Cluff Lake and Rio Algom Sludge

	Sample Identification			
Element	Rio Algom Bottle 2 (mg/L)	Rio Algom Bottle 14 (mg/L)	Cluff Lake Bottle 1 (mg/L)	Cluff Lake Bottle 6 (mg/L)
Sr	0.252 ±0.002	0.252 ±0.003	0.0756 ±0.0009	0.0688 ±0.0005
Ba	0.0293 ±0.0001	0.0233 ±0.0002	0.690 ±0.007	0.392 ±0.004
Al	B.D.L.	B.D.L.	0.0861 ±0.0007	0.0323 ±0.0003
B	0.0746 ±0.0005	0.0576 ±0.0006	0.287 ±0.003	0.266 ±0.004
Mn	0.733 ±0.007	0.578 ±0.006	7.32 ±0.07	6.09 ±0.06
Fe	0.0289 ±0.0002	0.0430 ±0.0003	0.342 ±0.003	0.103 ±0.001
S	423±3	428±2	184±2	324±2
Mg	3.82 ±0.02	4.01 ±0.04	99.3 ±0.1	93.6 ±0.1
As	B.D.L.	B.D.L.	0.1640 ±0.0003	0.0902 ±0.0004
V	B.D.L.	B.D.L.	B.D.L.	0.0103 ±0.0001
Na	1.27 ±0.02	1.20 ±0.03	191 ±3	177 ±2
Mo	B.D.L.	B.D.L.	0.0265 ±0.0002	0.0281 ±0.0001
Ca	539±2	540±2	204±2	210±1
Zn	0.0120 ±0.0002	0.00649 ±0.00014	0.00565 ±0.00013	B.D.L.
Li	0.309 ±0.004	0.292 ±0.009	B.D.L.	B.D.L
K	94.7 ±0.2	95.2 ±0.3	14.4 ±0.1	15.2 ±0.1
Si	-	2.42 ±0.04	0.110 ±0.002	0.140 ±0.006

[a] B.D.L. denotes Below Detection Limit. See Appendix 2.3 for detection limits.

Table 7. Average Concentrations for Measured Elements in Cluff Lake and Rio Algom Sludge Samples

	Major Elements, expressed as percent							Trace Elements, expressed as µg per g (ppm)*								
Bottle #	Ba	S	Al	Ca	Fe	Sr	K	Mg	Mn	Zn	B	Cu	Pb	V	Cr	^{226}Ra
RA 2	42.5	14.4	2.67	4.03	3.90	0.380	0.325	336	332	397	173	130	268	16.5	24.4	1284
RA 14	44.5	15.8	2.64	3.99	4.20	0.378	0.329	507	329	325	430	164	341	21.0	28.1	1431
CL 6	40.0	14.8	6.86	1.32	0.74	0.296	0.388	1750	593	362	100	64.2	540	53.0	31.0	701
CL 18	39.1	22.4	8.04	1.40	0.78	0.285	0.617	2327	596	542	326	174	768	78.1	47.9	678
A2	32.9	18.5	6.71	4.21	1.43	0.157	0.175	1261	228	1223	128	99.3	301	13.6	20.4	-
A1	38.8	19.8	6.75	3.13	1.22	0.173	0.284	926	189	1083	205	111	512	46.3	14.6	-

* Except radium-226 which is expressed in Bq/g.

In the dissolution procedure, the red precipitate characteristic of hydrous iron oxide was observed in the Rio Algom samples but not in the Cluff Lake samples. The ICP analysis showed a much higher iron content of approximately 4% for the Rio Algom samples as compared to the approximately 0.75% found in the Cluff Lake samples.

Significant differences were noted in the calcium, magnesium and aluminum concentrations of the sludges from the two mines. For Cluff Lake the calcium, magnesium and aluminum concentrations were 1.4%, 0.21% and 7.5% respectively compared to 4%, 4% and 0.05% respectively for the Rio Algom sludge.

For the lime treated sludge samples, considerable variation was noted between individual subsamples for all elements. The addition of lime has apparently introduced a large variability in composition. The iron content of the Cluff Lake samples not treated with lime is quite low, about 0.75%. In comparison, the concentration in the lime treated samples is approximately double, on the order of 1.4%. Since lime is predominantly calcium carbonate the calcium content should be much higher in the lime treated samples and this was found to be the case. The calcium concentration in the lime treated samples was found to be approximately 4% compared to 1.5% for the untreated samples. Although magnesium carbonate is usually present in lime, the magnesium concentration (0.1%) was lower in the lime treated samples than in the untreated samples (0.2%). The supernatant solution for the lime treated samples was not analyzed. It would be expected, however, that the magnesium concentration would be higher in the lime treated supernatants than in the untreated supernatants.

7.0 GEOCHEMICAL MODELLING

7.1 Procedures

7.1.1 Geochemical Modelling with the SLUDGE Program

The geochemical code SLUDGE was designed and implemented to assess three of the main factors relevant to $^{226}Ra^{2+}$ leachability. The FORTRAN computer code is presented in Appendix 3.1. Simulations with the model were run first on the University of Alberta's Amdahl 580 computer and later on an IBM-PC.

SLUDGE was selected for initial investigation because it is a relatively simple program (when compared to the PHREEQE program used later in this study). It is, therefore, easier to identify and understand the $BaSO_{4(s)}$ dissolution mechanisms which would require more complex evaluation.

SLUDGE and PHREEQE were expected to agree and did, providing independent validation of each code.

7.1.1.1 Description of the Model

SLUDGE simulates a simple case of batch leaching with the dissolution of $(Ba,Ra)SO_4$ sludge in an aqueous solution. The model is based on the assumption that all of the $^{226}Ra^{2+}$ in the sludge is co-precipitated with $BaSO_{4(s)}$ and that the solubility of this co-precipitate, $(Ba,Ra)SO_4$, is equivalent to the solubility of $BaSO_{4(s)}$. The computer code calculates the quantity of $BaSO_{4(s)}$ that would dissolve in one kilogram of a solution consisting of water, sulfur and barium. The code then calculates the quantity of $^{226}Ra^{2+}$ dissolved in the solution, based on the amount of $(BaSO_{4(s)}$ dissolved.

To conduct a simulation with SLUDGE the user inputs the desired ionic strength, pH, total sulfur concentration (in mol/kg) and Ba^{2+} concentration (in mol/kg) of the initial solution. The computer code then calculates the following:

1. activity coefficients for monovalent and divalent aqueous species.
2. the SO_4^{2-} and HSO_4^- concentrations from the total sulfur concentration and the pH, assuming that the total sulfur is partitioned between SO_4^{2-} and HSO_4^- only.
3. the ion activity product (IAP) for $BaSO_{4(s)}$.
4. the saturation state of the solution with respect to $BaSO_{4(s)}$.
5. if the solution is undersaturated, the amount of $BaSO_{4(s)}$ that has to be dissolved in order to achieve saturation (thermodynamic equilibrium)
6. on the basis of 5, the quantity of $^{226}Ra^{2+}$ released into the solution, assuming the $BaSO_{4(s)}$ has a known $^{226}Ra^{2+}$ activity.

The $^{226}Ra^{2+}$ activity used in our simulations was 1,062 Bq/g. This is the activity of the 1980 Elliot Lake sludge reported by Huck and Anderson (6).

7.1.1.2 Design of Simulation Experiments

Simulations with SLUDGE evaluated the variations in $^{226}Ra^{2+}$ release caused by changes in the SO_4^{2-} concentration, the Ba^{2+} concentration and the ionic strength of a specified solution. These computer trials replicated in a general way the experimental work of Huck and Anderson (6). Three sets of simulations were run. For the first set, the concentration of total sulfur was varied by orders of magnitude between 10^{-7} and 10^{-3} mol/kg. This range is equivalent to 0.0032 to 32 mg/kg total sulfur. The concentration of Ba^{2+} was varied in the second set using the same mol/kg range of values, which in this case corresponds to 0.0137 to 137 mg/kg barium. In the third set, values of ionic strength of 0.0, 0.001, 0.01 and 0.1 were used. Values below 0.001

represent very dilute solutions; the ionic strength of surface water is typically in the order of 0.01, while that of shallow groundwater usually ranges between 0.01 and 0.1. The base values chosen for the four program variables were 0.0 for ionic strength, 7.0 for pH and 10^{-7} mol/kg for the Ba^{2+} and total sulfur concentrations.

The objective of the simulations was to determine trends in $^{226}Ra^{2+}$ leaching. No attempt was made to reproduce actual numerical results obtained from laboratory batch leaching experiments.

7.1.2 Geochemical Modelling with the PHREEQE Program

7.1.2.1 General Statement

The leaching of $^{226}Ra^{2+}$ from $(Ba,Ra)SO_4$ sludge is a complex geochemical process. Although SLUDGE is useful for understanding the role that several controlling chemical parameters play in this phenomenon, it can not account for the geochemical processes involving multicomponent, multiphase equilibria that operate in real settings. Consequently, a more sophisticated aqueous chemical model and computer code is required. The majority of existing aqueous models use ion-association concepts which are implemented in a variety of computer programs. The programs currently in use can be divided into two basic types: those determining equilibrium speciation and those simulating non-equilibrium reaction progress. To gain a better understanding of $^{226}Ra^{2+}$ leaching under laboratory and field conditions we used a non-equilibrium reaction progress model.

7.1.2.2 Description of PHREEQE

The program chosen for use in this study is called PHREEQE (PH, REdox, EQuilibrium Equations). PHREEQE is a non-equilibrium reaction progress program that is based on an ion-association aqueous model. It is a FORTRAN computer code developed by the U.S. Geological Survey (25) that was designed to deal with problems of surface and groundwater hydrochemistry. The specific purpose of PHREEQE is to simulate geochemical reactions. The reactions can be one or a combination of the following:

1. addition of reactants to a solution
2. mixing of two or more solutions
3. titrating one solution with another

In each case PHREEQE can simultaneously maintain reacting solutions at equilibrium with multiple phase boundaries and calculate the composition of the aqueous phase. Mass transfer as a function of reaction progress quantitatively documents the transfer of mass between the solid and aqueous phases.

PHREEQE was obtained and adapted to the University of Alberta's Amdahl 580 computer. The thermodynamic data base used by the program was examined for errors and augmented to include the elements, aqueous species and mineral phases that are relevent to this study (26). To facilitate the preparation of data sets for the various simulations, we obtained and adapted an interactive preformatting program called PHRQIN. This program was written by Fleming and Plummer of the U.S. Geological Survey in 1980.

Listings of the PHREEQE code, the thermodynamic data base used in PHREEQE and the PHRQIN code are given in Appendices 3.2, 3.3 and 3.4. The computer operations procedure designed to use these codes and the data base with the University of Alberta's computer facilities are summarized in Appendix 3.5. A detailed summary of the theory, features and use of PHREEQE is given in the user's manual prepared by Parkhurst et al. (25). A user's manual is not available for the PHRQIN program.

The PHREEQE program is not a copyright package. Additional information about the program can be obtained from:

U.S. Geological Survey
National Center
Office of the Regional Hydrologist
MS 432
Reston, Virginia
U.S.A., 22092

Information on card decks can be obtained from:

Ralph N. Eicher
U.S. Geological Sirvey
National Center
Office of the Regional Hydrologist
MS 432
Reston, Virginia
U.S.A., 22092

7.1.2.3 Overview of a PHREEQE Simulation

Before discussing the simulations conducted with PHREEQE it is instructive to examine briefly a typical model simulation conducted in this study. The user first establishes various reaction criteria referred to as input options which determine the methods to be used for the calculation of pH and pe, the type of reaction to be simulated, temperature criteria, etc. Next, the user indicates the number of reaction steps that will occur, the number of constituents included in a net stoichiometric reaction, the chemical and physical characteristics of the solution and the chemical characteristics of the reacting mineral (e.g. $BaSO_{4(s)}$). Finally, any mineral phases to be maintained at equilibrium with the solution are specified.

For the given input data the computer code calculates the following:

1. pH (if not previously specified),
2. pe (if not previously specified),
3. the total concentrations of elements in the initial and final solutions,
4. the amounts of minerals (or other phases) transferred into or out of the aqueous phase,
5. the distribution of aqueous species in the initial and final solutions, and
6. the saturation state of the aqueous phase with respect to specified mineral phases.

The output consists of a summary of the input data and the results of the calculations.

A complete example of a PHREEQE simulation is given in Appendix 3.6.

7.1.2.4 Geochemical Simulations Conducted with PHREEQE

PHREEQE was used to conduct six groups of geochemical simulations. A summary of the procedure used for each group is given in the following sections.

7.1.2.4.1 Comparison of SLUDGE and PHREEQE Model Results

The first trials with PHREEQE were designed to replicate the first two experiments previously conducted with SLUDGE in order to compare the results of both models. Four simulations were required to run each experiment. In the first set the concentration of total sulfur was varied between 10^{-6} and 10^{-3} mol/kg while for the second set the concentration of Ba^{2+} was varied between 10^{-6} and 10^{-3} mol/kg. Again, the default value used for the total sulfur and Ba^{2+} concentrations was 10^{-7} mol/kg and the default pH was 7.0. PHREEQE calculates a value for ionic strength and therefore the specification of a default value was not required.

7.1.2.4.2 Assessing Radium-226 Release at Various pH Values

The results of the batch leaching experiments conducted by Huck and Anderson (6) demonstrated that low and high values of pH increased the leaching of $^{226}Ra^{2+}$ from 1981 Elliot Lake sludge, with solutions of low pH being the strongest leachants. Our second group of simulations investigated whether this enhanced leaching could be replicated using PHREEQE. For each of seven simulations a solution consisting of water, 10^{-7} mol/kg total sulfur and 10^{-7} mol/kg Ba^{2+} was assigned a pH value of 1.0, 3.0, 5.0, 7.0, 9.0, 11.0 or 13.0. The pH of each solution was fixed by "adding" either acid or base (denoted in the model by Cl^- and Na^+ respectively). For each solution the program calculated the moles of $BaSO_{4(s)}$ that would have to be dissolved in order to reach saturation for this mineral. The quantity of $^{226}Ra^{2+}$ that would be dissolved was then calculated manually by assuming that the $BaSO_{4(s)}$ had a $^{226}Ra^{2+}$ activity of 1062 Bq/g.

The objective of this exercise was to reproduce the observed trends in the data reported by Huck and Anderson (6). We did not attempt to reproduce the actual numerical results.

7.1.2.4.3 Simulation of Batch Leaching Experiments

PHREEQE was used to simulate batch leaching experiments similar to those conducted by Huck and Anderson (6). The objective was to predict the quantity of $^{226}Ra^{2+}$ that would be leached from a specified amount of 1980 Elliot Lake sludge by "reacting" the sludge with one kilogram of distilled water. The mineralogy of the 1980 sludge used in the simulations was reported by Skeaff and Campbell (10) and by Huck and Anderson (6). The simulation procedure was to react very small amounts of sludge with one kilogram of distilled water in steps until the solution became slightly oversaturated with respect to $BaSO_{4(s)}$. This determined the amount of sludge dissolution required to reach saturation with respect to $BaSO_{4(s)}$. The $^{226}Ra^{2+}$ release was then calculated from the assumed $^{226}Ra^{2+}$ activity of the sludge. Two simulations were conducted with this procedure. In the first, the solution was permitted to become oversaturated with respect to mineral phases other than $BaSO_{4(s)}$ while in the second, mineral phases were allowed to precipitate before saturation with $BaSO_{4(s)}$ was reached.

It was our original intention to conduct these simulations using the mineralogical characteristics of a Cluff Lake sludge sample and a sample of 1981 Elliot Lake sludge. Samples of both sludges were submitted to Dr. F. Longstaffe of the University of Alberta's Geology Department for mineralogical analysis using X-Ray Diffraction (XRD) techniques. The results of the analyses indicated that both samples consisted of essentially 100% $BaSO_{4(s)}$. Both may have had traces of quartz, and the Elliot Lake sample also may have had a trace of calcite. These results for the 1981 Elliot Lake sample do not agree with the mineralogical composition of the 1980 sample reported by Skeaff and Campbell (10) and Huck and Anderson (6). The discrepancy may be related to the fact that XRD analysis will not detect amorphous compounds; such compounds may be present in the 1981 Elliot Lake sample and, perhaps, the Cluff Lake sample. In view of the uncertainty, it was decided to perform the above simulations only with the mineralogical composition reported for the 1980 Elliot Lake sludge sample.

7.1.2.4.4 Evaluation of $BaSO_{4(s)}$ Stability Under Various pe-pH Conditions

In the fourth group of simulations PHREEQE was used to calculate aqueous speciation and the thermodynamic stability of $BaSO_{4(s)}$ under various pH and pe conditions. The objective was to determine whether the results provided by PHREEQE would be the same as those obtained using traditional methods, i.e. by the preparation of a stability or Pourbaix diagram.

A pe-pH diagram showing the equilibrium stability relationships of the Ba-S-O-H_2O system at 25°C (Figure 3) illustrates the important extent to which pe and pH determine the speciation and the stability of $BaSO_{4(s)}$. To prepare the figure the concentrations of Ba^{2+} and total sulfur (Σ S) were assigned activity values of 10^{-4}. Total sulfur is partitioned between SO_4^{2-}, HSO_4^-, H_2S and HS^-, and barium occurs as the free ion (Ba^{2+}) or in the mineral phase $BaSO_{4(s)}$. The most important feature of the diagram in terms of the dissolution of $BaSO_{4(s)}$ is the shaded region. Within this region reducing conditions exist in which $BaSO_{4(s)}$ is not stable because the dominant sulfur species are H_2S and HS^-. $BaSO_{4(s)}$ will be stable outside this region because oxidizing conditions exist in which the dominant sulfur species is SO_4^{2-}. The

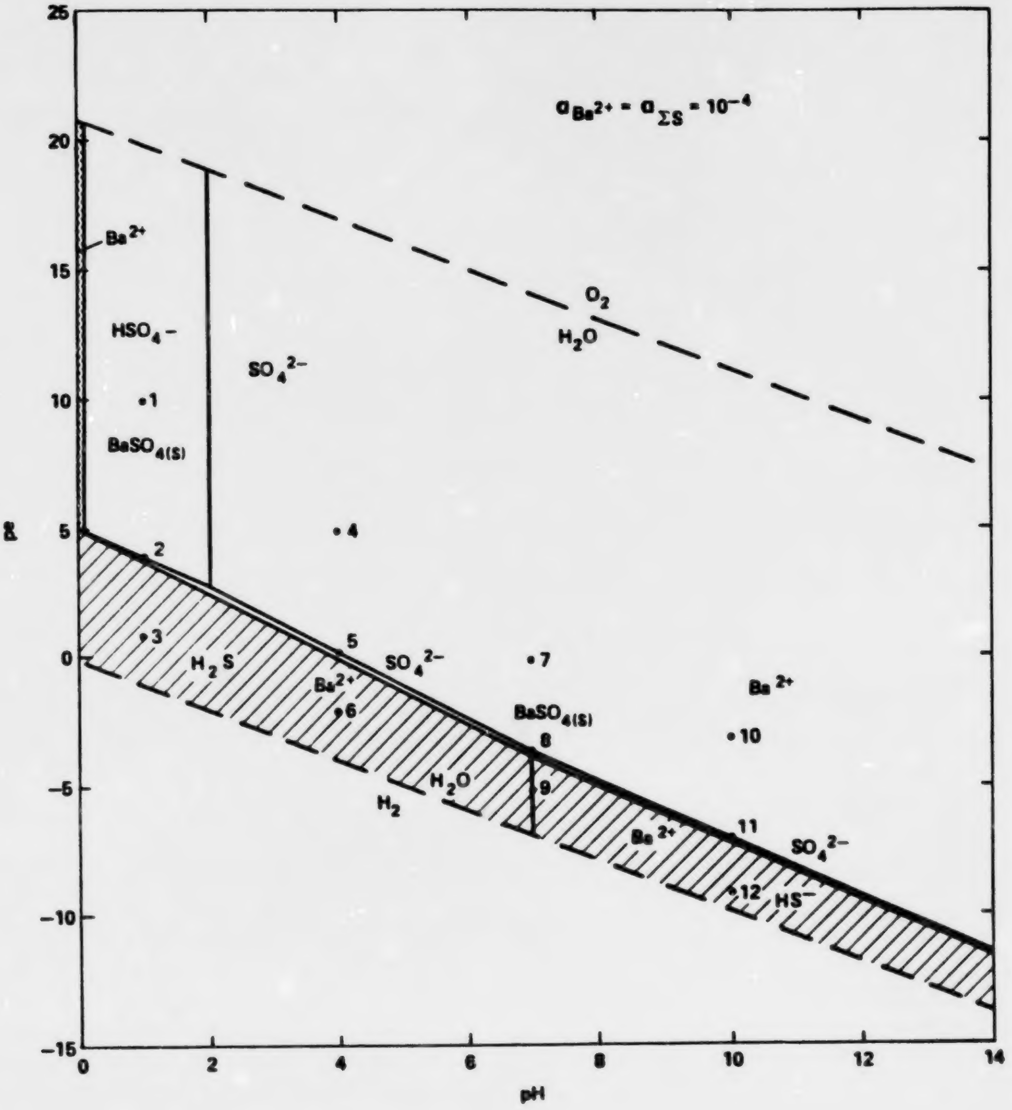


Figure 3. Ba-S-O-H_2O System Stability Relationships.

only exception is the pe-pH region indicated by the shading at the extreme left of the diagram where barium will exist only as a free ion and consequently, $BaSO_{4(s)}$ will not be stable.

The stability diagram shown in Figure 3 was prepared using standard geochemical methods. To determine whether PHREEQE could predict the stability fields shown in Figure 3, simulations for 12 different pe-pH combinations were conducted. These 12 pe-pH pairs are indicated in Figure 3. The procedure used for each simulation was the same: a solution consisting of distilled water, 10^{-4} mol/kg sulfur and 10^{-4} mol/kg Ba^{2+}, and an assigned pair of pe and pH values was specified; the program then performed speciation calculations and determined the saturation state of the solution with respect to $BaSO_{4(s)}$.

7.1.2.4.5 Stability of $BaSO_{4(s)}$ in Water with and without Dissolved Oxygen

Two sets of simulations were conducted to compare the quantity of $BaSO_{4(s)}$ that would dissolve in waters with and without dissolved oxygen. The objective was to simulate, in general terms, the effect of storing sludge in oxidizing and reducing groundwater environments. The design of the simulations was the same as that used to simulate batch leaching. In the first set, one kilogram of distilled water was assigned a pH of 7.0 and a pe of 0, thereby representing an O_2-containing water. $BaSO_{4(s)}$ was then "added" to the water in steps until saturation was slightly exceeded. For the second set, the same procedure was used except that pe was assigned a value of -5 in order to produce an O_2-free water.

7.1.2.4.6 Dissolution of $BaSO_{4(s)}$ in Three Hypothetical Solutions

One of the most powerful applications of the PHREEQE program is to model the geochemical environment of a real or hypothetical hydrogeologic system.

It is beyond the scope of this study to use the program to simulate possible sludge disposal settings but its utility in investigating potential disposal schemes can be demonstrated. In the last group of simulations PHREEQE was used to illustrate how the program could predict in a general way the stability of $(Ba,Ra)SO_4$ sludge placed in a tailings basin.

The dominant mineral controlling the geochemistry of several tailings basins currently in use in Ontario is pyrite (5). The tailings are generally positioned above or just below the water table, i.e. in an environment where oxidizing conditions prevail. In this environment the oxidation of pyrite by oxygen will occur (27), resulting in the leachate being dominated by Fe^{2+}, SO_4^{2-} and very low pH. The governing equation for the oxidation reaction is:

$$FeS_2 + 3O_2 + 2H_2O = Fe^{2+} + 2SO_4^{2-} + 4H^+$$

If $(Ba,Ra)SO_4$ sludge were to be placed in a pyritic tailings basin, the stability of the sludge in contact with a leachate dominated by the products of pyrite oxidation must be considered.

Three simulations were run to assess the solubility of $BaSO_{4(s)}$ in leachate generated under conditions involving pyrite oxidation. For the first simulation, the irreversible reaction of oxygen with pyrite was modelled in five steps. The initial solution was distilled water, pyrite equilibrium was maintained throughout the entire simulation and the five steps were comprised of the reaction of 0.0, 0.001, 0.005, 0.01 and 0.05 moles of oxygen with the solution. The total amount of iron in solution was controlled by hematite equilibrium - that is, hematite was added to or precipitated from the solution, depending on the saturation state. At the end of each step the amount of $BaSO_{4(s)}$ that had to be dissolved for the solution to reach saturation with this mineral was determined. The program calculated the solution composition, pH, pe and mass transfer of pyrite, hematite and $BaSO_{4(s)}$ at 25°C for each step. The quantity of $^{226}Ra^{2+}$ that would be released to the solution was calculated manually on the basis of the amount of $BaSO_{4(s)}$ dissolved and a sludge $^{226}Ra^{2+}$ activity level of 1062 Bq/g. It should be noted that adding 0.0 moles of oxygen in the first step established the equilibrium composition of the closed system (i.e. no oxidation of pyrite occurring).

The procedure for the second simulation was identical to that used for the first except that pH was buffered by equilibrium with calcite. The third simulation was the same as the second except that the total system was also in equilibrium with gypsum.

7.2 Results

7.2.1 Geochemical Modelling with the SLUDGE Progam

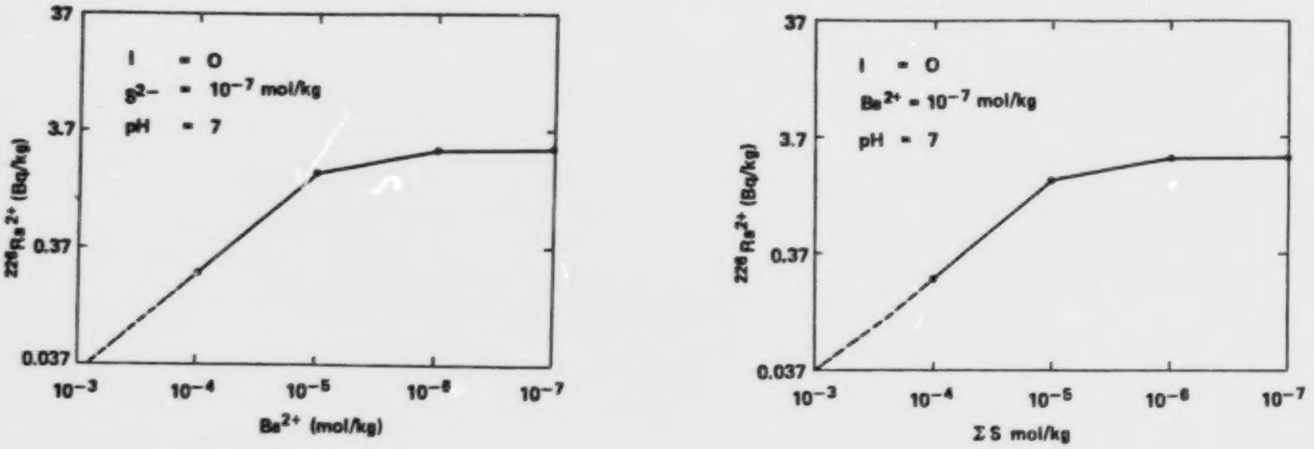
The geochemical model SLUDGE was used to simulate the effects of variations in solution ionic strength, Ba^{2+} concentration and SO_4^{2-} concentration on the leachability of $^{226}Ra^{2+}$ from $(Ba,Ra)SO_4$ sludge. The results of the three sets of simulations are shown in Table 8 and Figure 4.

The main factor controlling the leaching of $^{226}Ra^{2+}$ is the saturation state of the solution with respect to $BaSO_{4(s)}$. As expected, the results of the first and second simulations showed that increasing the concentration of either Ba^{2+} or SO_4^{2-} in a solution undersaturated with $BaSO_{4(s)}$ resulted in a decrease in the degree of undersaturation. Consequently, lesser amounts of $BaSO_{4(s)}$ could dissolve in the solution and smaller quantities of $^{226}Ra^{2+}$ were released. Once $BaSO_{4(s)}$ saturation is reached the release of $^{226}Ra^{2+}$ is

Table 8. Assessment of Four Factors Affecting $^{226}Ra^{2+}$ Leachability

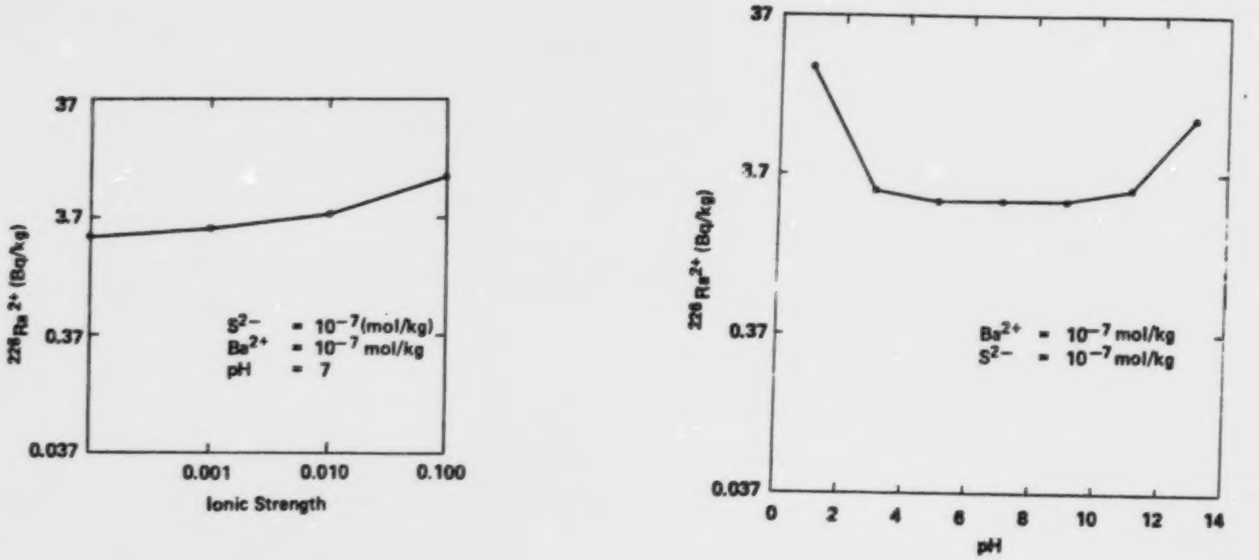
Geochemical Model	Simulation Set No.	Ionic Strength	Total Sulfur (mol/kg)	Ba^{2+} (mol/kg)	pH	Moles of $BaSO_{4(s)}$ Dissolved to Achieve Saturation	Radium-226 Concentration in Solution (Bq/kg)
SLUDGE	1	0.0	1E-7	1E-7	7.0	1.0 E-5	2.52
		0.0	1E-6	1E-7	7.0	9.7 E-6	2.41
		0.0	1E-5	1E-7	7.0	6.3 E-6	1.55
		0.0	1E-4	1E-7	7.0	9.0 E-7	0.22
		0.0	1E-3	1E-7	7.0	0.0	<0.04
SLUDGE	2	0.0	1E-7	1E-7	7.0	1.0 E-5	2.52
		0.0	1E-7	1E-6	7.0	9.7 E-6	2.41
		0.0	1E-7	1E-5	7.0	6.3 E-6	1.55
		0.0	1E-7	1E-4	7.0	9.0 E-7	0.22
		0.0	1E-7	1E-3	7.0	0.0	<0.04
SLUDGE	3	0.0	1E-7	1E-7	7.0	1.0 E-5	2.52
		0.001	1E-7	1E-7	7.0	1.2 E-5	2.89
		0.01	1E-7	1E-7	7.0	1.6 E-5	3.85
		0.1	1E-7	1E-7	7.0	3.3 E-5	8.18
PHREEQE	1	0.130	1E-7	1E-7	1.0	6.9 E-5	17.13
		0.001	1E-7	1E-7	3.0	1.2 E-5	2.92
		0.000	1E-7	1E-7	5.0	1.0 E-5	2.52
		0.000	1E-7	1E-7	7.0	1.0 E-5	2.52
		0.000	1E-7	1E-7	9.0	1.0 E-5	2.52
		0.001	1E-7	1E-7	11.0	1.2 E-5	2.92
		0.130	1E-7	1E-7	13.0	3.6 E-5	8.95

* based on a $^{226}Ra^{2+}$ activity of 1062 Bq per gram of $(Ba,Ra)SO_4$ sludge, represented as $BaSO_{4(s)}$



a. Effect of Ba^{2+} Concentration

b. Effect of Sulfur Concentration



c. Effect of Ionic Strength

d. Effect of pH

Figure 4. $^{226}Ra^{2+}$ Results for Simulations with SLUDGE halted.

The third variable evaluated by the model was ionic strength. In general terms, an increase in the ionic strength of a solution decreases the thermodynamic activity of the aqueous species because of ionic interactions and hydration shell effects. Consequently, if a solution is saturated with a mineral phase at one level of ionic strength, it will become undersaturated at higher ionic strengths. This phenomenon is illustrated by the results of simulation set No. 3. Increasing the ionic strength of the solution from 0.0 to 0.1 resulted in an increase in the degree of undersaturation with $BaSO_{4(s)}$. Therefore an increasing amount of $BaSO_{4(s)}$ had to dissolve in the solution to establish saturation conditions. This increased the amount of $^{226}Ra^{2+}$ released.

7.2.2 Geochemical Modelling with the PHREEQE Program

7.2.2.1 A Comparison of SLUDGE and PHREEQE Model Results

PHREEQE was used to replicate two of the theoretical experiments conducted with SLUDGE. Specifically, simulations were conducted with PHREEQE to assess the effects that variations in the concentrations of total sulfur and Ba^{2+} had on the solubililty of $BaSO_{4(s)}$ and to compare these results to those previously obtained with SLUDGE.

The results of the PHREEQE and SLUDGE simulations shown in Table 9 compare very favourably. The small discrepancies that exist are caused by different values of ionic strength used in each model. In the simulations with SLUDGE the ionic strength parameter was assigned a value of zero, whereas with PHREEQE values of ionic strength are calculated in the code to be greater than zero.

Table 9. Comparsion of SLUDGE and PHREEQE Model Results

Total Sulfur (mol/kg)	Ba^{2+} (mol/kg)	pH	Moles of $BaSO_{4(s)}$ Dissolved to Achieve Saturation		$^{226}Ra^{2+}$ Activity in Solution (Bq/kg)	
			SLUDGE	PHREEQE	SLUDGE	PHREEQE
1E-6	1E-7	7.0	9.7 E-6	1.0 E-5	2.41	2.52
1E-5	1E-7	7.0	6.3 E-6	6.7 E-6	1.55	1.67
1E-4	1E-7	7.0	9.0 E-7	1.1 E-6	0.22	0.26
1E-3	1E-7	7.0	<1.0 E-7	7.0 E-8	<0.04	<0.04
1E-7	1E-6	7.0	9.7 E-6	1.0 E-5	2.41	2.52
1E-7	1E-5	7.0	6.3 E-6	6.7 E-6	1.55	1.67
1E-7	1E-4	7.0	9.0 E-7	1.1 E-6	0.22	0.26
1E-7	1E-3	7.0	<1.0 E-7	7.0 E-8	<0.04	<0.04

7.2.2.2 Assessing Radium-226 Release at Various pH Values

It was noted previously that in the batch experiments conducted by Huck and Anderson (6) very low and very high pH values increased $^{226}Ra^{2+}$ activity levels in the leaching solutions. The results of the set of PHREEQE simulations designed to assess this phenomenon (Table 8) verified these laboratory observations. Varying the pH between 5.0 and 9.0 did not change the amount of $^{226}Ra^{2+}$ released to solution. However, for pH values of 3.0 and 11.0 the amount released increased slightly and with the extreme values of 1.0 and 13.0 the release was substantial.

The additional release of $^{226}Ra^{2+}$ at high pH values was caused by the increase in the ionic strength of the solution resulting from the addition of pH-controlling solutes. In the simulations a large amount of base (denoted as Na^+ in the program) to be added to the solution to fix the pH values of 11.0 and 13.0. In the experiments conducted by Huck and Anderson (6), the pH-controlling solute was NaOH. At low pH values increased $^{226}Ra^{2+}$ activity levels in solution were also caused by increases in the ionic strength created by the introduction of pH-controlling solutes. In the model simulations the pH values of 1.0 and 3.0 were fixed using HCl (denoted as Cl^- in the program), whereas either HCl or H_2SO_4 was used in the laboratory experiments.

Huck and Anderson (6) found that more $^{226}Ra^{2+}$ was leached at very low pH values than at very high values. This phenomenon is also apparent in the simulation results for pH 1.0 and pH 13.0. At pH levels greater than 2.0 the dominant sulfate species is SO_4^{2-} whereas at pH values less than 2.0 the total sulfate is partitioned between SO_4^{2-} and HSO_4^-. The production of HSO_4^- decreases the concentration of SO_4^{2-} in solution. The solution therefore becomes more undersaturated with $BaSO_{4(s)}$, and more $BaSO_{4(s)}$ will dissolve. This additional dissolution of $BaSO_{4(s)}$ results in increased

$^{226}Ra^{2+}$ activity levels in solution.

7.2.2.3 Simulation of Batch Leaching Experiments

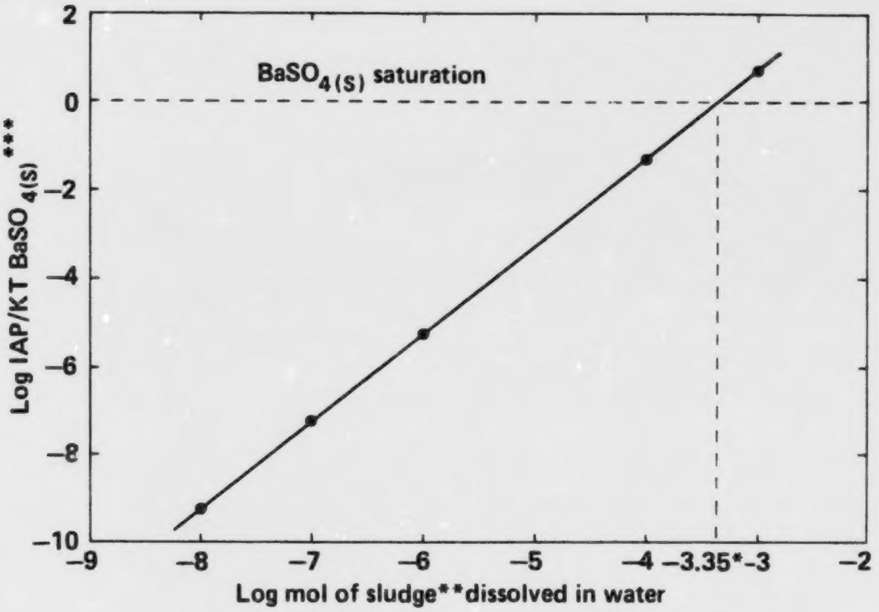
Two batch leaching experiments similar to actual experiments conducted by Huck and Anderson (6) were simulated by adding small increments of a hypothetical 1980 Elliot Lake sludge to distilled water until the solution became saturated with respect to $BaSO_{4(s)}$. In the first experiment the solution was allowed to become oversaturated with respect to hematite (Fe_2O_3) and gibbsite ($Al(OH)_3$), while in the second these two mineral phases were allowed to precipitate.

The results of the two experiments were the same and are illustrated in Figure 10. In both experiments, 0.00045 grams of sludge could dissolve in one kilogram of distilled water at 25°C. On the basis of a $^{226}Ra^{2+}$ activity level of 1062 Bq/g, this would release 0.48 Bq of $^{226}Ra^{2+}$ to solution.

7.2.2.4 Evaluation of $BaSO_{4(s)}$ Stability Under Various pe-pH Conditions

For 12 combinations of pe and pH PHREEQE was used to determine the speciation in a solution comprised of 10^{-4} mol/kg of Ba^{2+} and S in distilled water. The saturation state of the solution with respect to $BaSO_{4(s)}$ was also determined. This was done to verify that PHREEQE could provide representative results for future simulation experiments involving redox reactions.

The results of the simulations are shown in Tables 10a to 10d with the dominant sulfur species under each condition highlighted. The results demonstrate that the program was able to match the speciation shown on the Ba-S-O-H_2O stability diagram (Figure 3). For example, for a pH of 7 and a pe of 0 (simulation No. 7), the dominant sulfur species is SO_4^{2-}. Also for this pe-pH pair, $BaSO_{4(s)}$ is stable (log IAP/KT $BaSO_{4(s)}$ >0). Similarly, with pH



* log - 3.35 = 0.00045 g of sludge

** hypothetical compositions

*** negative values indicate undersaturation - positive values indicate oversaturation

Figure 5. Results of Simulated Batch Leaching Experiments.

Table 10a. Speciation of 10^{-4} mol $BaSO_4$ at pH 1 and Variable pe

	Simulation No.		
	1	2	3
pe	10	4	1
log IAP/KT* $BaSO_{4(s)}$	0.45	0.45	-21.04
ionic strength	0.0621	0.0621	0.0621

Aqueous Species	Species Concentrations**		
Ba^{2+}	1.0 E-4	1.0 E-4	1.0 E-4
$BaOH^+$	2.3 E-17	2.3 E-17	2.3 E-17
$BaSO_4^\circ$	3.0 E-10	3.0 E-10	n.c.
SO_4^{2-}	**1.6 E-5**	**1.6 E-5**	5.3 E-27
S^{2-}	n.c.***	8.9 E-25	2.9 E-22
HSO_4^-	**8.4 E-5**	**8.4 E-5**	2.7 E-26
HS^-	n.c.	3.9 E-13	1.3 E-10
H_2S	n.c.	3.0 E-7	**1.0 E-4**

* where IAP = Ion Activity Product
KT = Equilibrium constant

** reported as molality

*** not calculated

Table 10b. Speciation of 10^{-4} mol $BaSO_4$ at pH 4 and Variable pe

	Simulation No.		
	4	5	6
pe	5	0.25	-2
log IAP/KT $BaSO_{4(s)}$	1.89	1.87	-14.70
ionic strength	0.0004	0.0004	0.0003

Aqueous Species	Species Concentrations*		
Ba^{2+}	1.0 E-4	1.0 E-4	1.0 E-4
$BaOH^+$	4.1 E-14	4.1 E-14	4.2 E-14
$BaSO_4°$	8.4 E-9	8.0 E-9	2.1 E-25
SO_4^{2-}	**9.9 E-5**	**9.5 E-5**	2.4 E-21
S^{2-}	n.c.**	5.2 E-18	1.3 E-16
HSO_4^-	8.9 E-7	8.6 E-7	2.2 E-23
HS^-	n.c.	4.0 E-9	1.0 E-7
H_2S	n.c.	3.8 E-6	**1.0 E-4**

* reported as molality

** not calculated

Table 10c. Speciation of 10^{-4} mol $BaSO_4$ at pH 7 and Variable pe

	Simulation No.		
	7	8	9
pe	0	-3.5	-5
log IAP/KT $BaSO_{4(s)}$	1.90	1.86	-9.01
ionic strength	0.0004	0.0004	0.0002

Aqueous Species	Species Concentrations*		
Ba^{2+}	1.0 E-4	1.0 E-4	1.0 E-4
$BaOH^+$	4.1 E-11	4.1 E-11	4.2 E-11
$BaSO_4^\circ$	8.5 E-9	7.9 E-9	1.1 E-19
SO_4^{2-}	**1.0 E-4**	**9.2 E-5**	1.2 E-15
S^{2-}	n.c.**	5.0 E-12	6.5 E-11
HSO_4^-	9.1 E-10	8.4 E-10	1.1 E-20
HS^-	n.c.	3.9 E-6	**5.1 E-5**
H_2S	n.c.	3.7 E-6	**4.9 E-5**

* reported as molality

** not calculated

Table 10d. Speciation of 10^{-4} mol $BaSO_4$ at pH 10 and Variable pe

	Simulation No.		
	10	11	12
pe	-3	-7	-9
log IAP/KT $BaSO_{4(s)}$	1.89	1.74	-13.72
ionic strength	0.0005	0.0004	0.0003

Aqueous Species	Species Concentrations*		
Ba^{2+}	1.0 E-4	1.0 E-4	1.0 E-4
$BaOH^+$	4.1 E-8	4.1 E-8	4.1 E-8
$BaSO_4°$	8.4 E-9	6.0 E-9	2.0 E-24
SO_4^{2-}	**1.0 E-4**	**7.0 E-5**	2.4 E-20
S^{2-}	n.c.**	3.8 E-8	1.3 E-7
HSO_4^-	9.0 E-13	6.4 E-13	2.2 E-28
HS^-	n.c.	**3.0 E-5**	**1.0 E-4**
H_2S	n.c.	2.8 E-8	9.6 E-8

* reported as molality

** not calculated

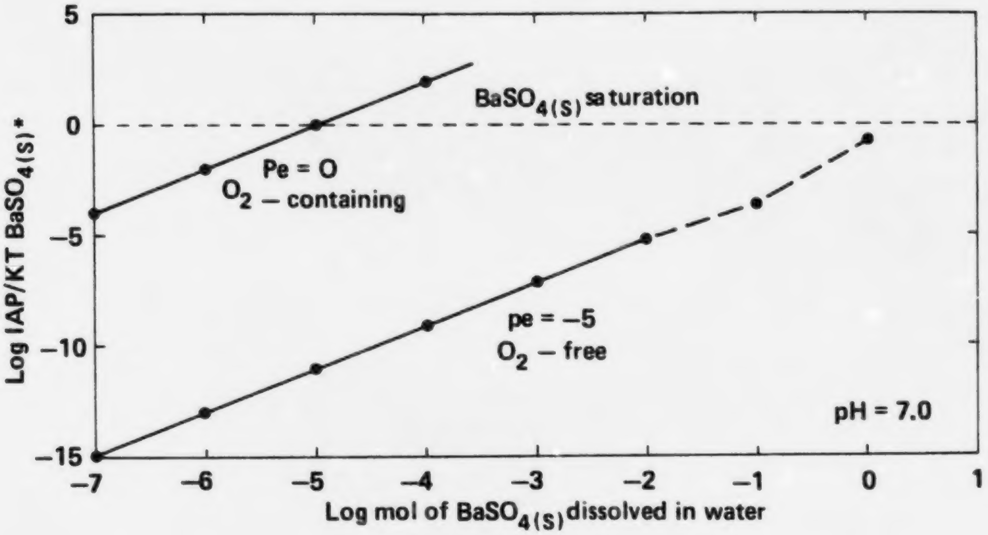
and pe values of 7 and -5 respectively (simulation No. 9), H_2S and HS^- are the dominant sulfur species, and $BaSO_{4(s)}$ is not stable (log IAP/KT $BaSO_{4(s)}$ <0). It is important to remember that the results in the tables apply to Ba^{2+} and sulfur concentrations of 10^{-4} mol/kg. Some differences will occur at other concentrations, but the overall pattern will remain the same.

7.2.2.5 Stability of $BaSO_{4(s)}$ in Water With and Without Dissolved Oxygen

Two sets of simulations were run to assess the saturation-state characteristics of $BaSO_{4(s)}$ in water with and without dissolved oxygen. The results of both sets are shown in Figure 6. The water containing dissolved oxygen becomes saturated with $BaSO_{4(s)}$, and from an equilibrium point of view, no further dissolution of $BaSO_{4(s)}$ can occur. For the O_2-free water, saturation with respect to $BaSO_{4(s)}$ did not occur. Theoretically, an infinite amount of $BaSO_{4(s)}$ can dissolve without saturation being reached, because the sulfate is continuously removed by reduction. The dashed line shown for the O_2-free water indicates that uncertainty exists in the results obtained for more than 10^{-2} mol $BaSO_{4(s)}$. This uncertainty is due to the very high ionic strength the solution created by these amounts of $BaSO_{4(s)}$. At these ionic strengths the equations used in PHREEQE to calculate the activity coefficients of the aqueous species become inaccurate.

In summary, the results demonstrate that:

1. an O_2-containing water undersaturated with $BaSO_{4(s)}$ will dissolve this mineral until saturation has been reached, and
2. an O_2-free water undersaturated with $BaSO_{4(s)}$ will not reach saturation, and therefore a large quantity of $BaSO_{4(s)}$ will dissolve. The actual amount that will dissolve and the rate of reduction can not be predicted by the PHREEQE model.



* negative values indicate undersaturation – positive indicate oversaturation

Figure 6. Saturation State of $BaSO_{4(s)}$ in Water With and Without Dissolved Oxygen

7.2.2.6 Dissolution of $BaSO_{4(s)}$ in Three Hypothetical Solutions

In the final set of simulations, the dissolution of $BaSO_{4(s)}$ was examined under three different chemical conditions involving the oxidation of pyrite by oxygen. These simulations were run to demonstrate by simple examples how the PHREEQE program might be of use in evaluating potential sludge disposal schemes. The three conditions used in the simulations were:

1. the oxidation of pyrite in water by oxygen with hematite equilibrium controlling the total iron concentration in solution,
2. the same as (1) but with pH buffered by equilibrium with calcite, and
3. the same as (2) but with the solution also buffered by equilibrium with gypsum.

The results of the simulations are given in Table 11 and Figure 7.

The results of the first simulation indicate that the dissolution of $BaSO_{4(s)}$ will be strongly affected by the oxidation of pyrite. The number of moles of $BaSO_{4(s)}$ dissolved in a closed system is predicted to be 1.1×10^{-5}. In the closed system pyrite is in equilibrium with the solution but oxidation of the pyrite has not occurred because of the absence of oxygen. The extent of $BaSO_{4(s)}$ dissolution decreases substantially to 3.4×10^{-8} mol/L as the oxidation of pyrite proceeds due to the production of SO_4^{2-}, as indicated in the governing reaction:

$$2\ FeS_2 + 7\ O_2 + 2H_2O = 2\ Fe^{2+} + 4\ SO_4^{2-} + 4H^+$$

In addition to the generation of Fe^{2+} and SO_4^{2-} the oxidation process also produces H^+ which is reflected in the decrease of pH from 7.2 to 4.0.

The results of the second simulation were similar to those for the first. The amount of BaSO4(s) dissolved in the closed system was the same but

Table 11. Results of Hypothetical $^{226}Ra^{2+}$ Leaching Simulations in Three Hypothetical Solutions

Simulation No.	Moles of O_2 Reacted with Solution	pH	pe	Ionic Strength	Total Fe^{2+} (mol/kg)	Total Ba^{2+} (mol/kg)	SO_4^{2-} (mol/kg)	$BaSO_{4(s)}$ Dissolved in Solution		$^{226}Ra^{2+}$ Activity in Solution (Bq/kg)
								(moles)	(grams)	
1	0.0	7.2	-3.3	0.000	5.8 E-8	1.1 E-5	1.1 E-5	1.1 E-5	2.6 E-3	2.78
	0.001	4.8	-0.1	0.002	6.0 E-4	2.8 E-7	5.8 E-4	2.8 E-7	6.5 E-5	0.07
	0.005	4.4	0.4	0.010	3.0 E-3	9.4 E-8	2.6 E-3	9.4 E-8	2.2 E-5	<0.04
	0.01	4.3	0.6	0.019	6.1 E-3	6.5 E-8	4.8 E-3	6.5 E-8	1.5 E-5	<0.04
	0.05	4.0	1.1	0.079	3.1 E-2	3.4 E-8	2.0 E-2	3.4 E-8	7.9 E-6	<0.04
2	0.0	9.9	-6.8	0.000	4.6 E-12	1.1 E-5	1.1 E-5	1.1 E-5	2.6 E-3	2.78
	0.001	8.0	-4.1	0.003	2.1 E-9	3.7 E-7	4.8 E-4	3.7 E-7	8.6 E-5	0.07
	0.005	7.0	-2.7	0.014	1.4 E-7	1.3 E-7	2.0 E-3	1.3 E-7	3.0 E-5	<0.04
	0.01	6.6	-2.3	0.023	6.2 E-7	9.0 E-8	3.8 E-3	9.0 E-8	2.1 E-5	<0.04
	0.05	6.0	-1.4	0.079	1.2 E-5	4.2 E-8	1.6 E-2	4.2 E-8	9.8 E-6	<0.04
3	0.0	9.1	-5.3	0.041	5.1 E-11	4.4 E-8	1.0 E-2	4.4 E-8	1.0 E-5	<0.04
	0.001	7.3	-3.1	0.041	5.3 E-8	4.6 E-8	1.0 E-2	4.6 E-8	1.1 E-5	<0.04
	0.005	6.7	-2.4	0.043	5.1 E-7	4.8 E-8	9.6 E-3	4.8 E-8	1.1 E-5	<0.04
	0.01	6.5	-2.1	0.044	1.2 E-6	5.1 E-8	9.3 E-3	5.1 E-8	1.2 E-5	<0.04
	0.05	6.0	-1.5	0.051	7.7 E-6	6.1 E-8	8.3 E-3	6.1 E-8	1.4 E-5	<0.04

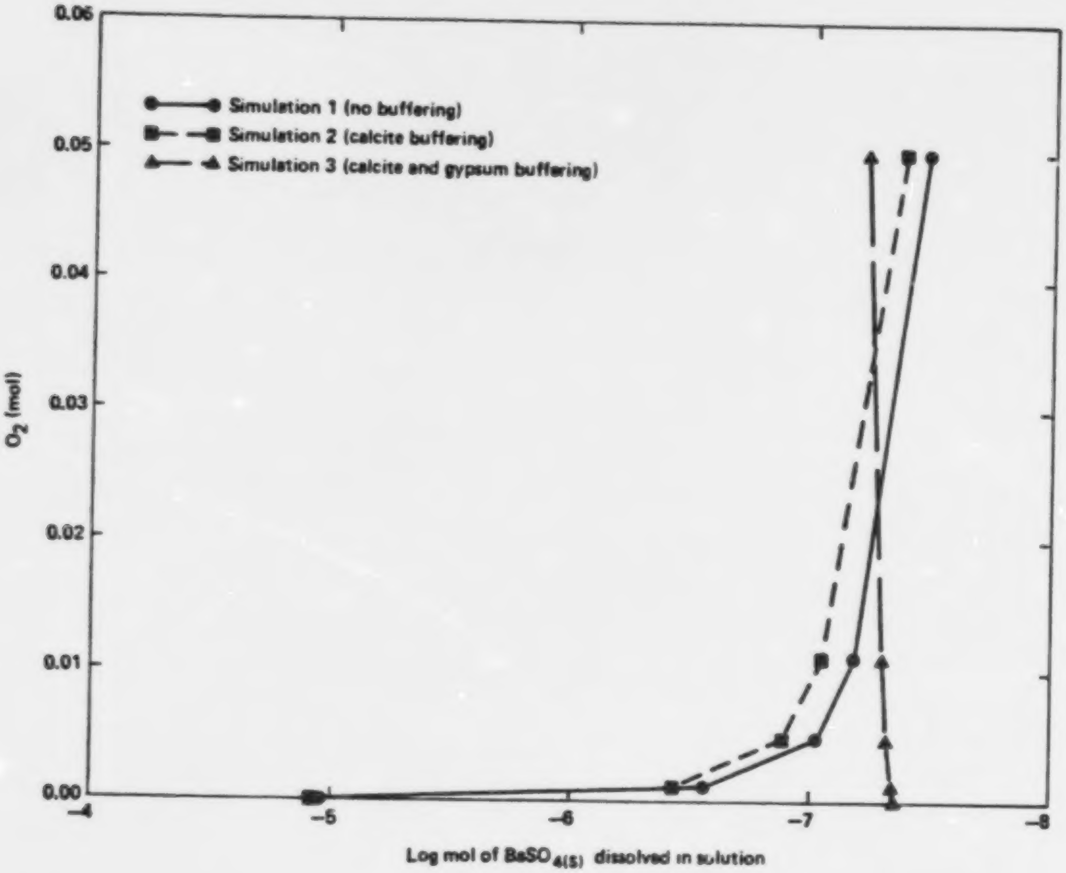


Figure 7. Dissolution of $BaSO_{4(s)}$ in Solutions Undergoing Pyrite Oxidation

as the oxidation process advanced the amount of $BaSO_{4(s)}$ dissolution that occurred is slightly less. This reduction is due to the change in the redox condition of the solution created by the buffering effect of calcite on pH. Consequently, the addition of calcite to the system will slightly retard the oxidation reaction.

The results of the third simulation demonstrate that buffering the system with gypsum minimizes the amount of $BaSO_{4(s)}$ dissolved. In the previous simulations the production of SO_4^{2-} by oxidation greatly reduced $BaSO_{4(s)}$ dissolution. However, in this simulation a substantial concentration of SO_4^{2-} exists in the solution before the oxidation reaction begins because of the dissolution of gypsum. Consequently, only minimal amounts of $BaSO_{4(s)}$ can dissolve. The results also illustrate that the amount of $BaSO_{4(s)}$ dissolved will increase slightly as the oxidation process advances. This small increase is the result of the increasing ionic strength of the solution.

Implications of the results on the disposal of sludge are evident after examining the $^{226}Ra^{2+}$ concentrations in Table 11. The results indicate that significant leaching of $^{226}Ra^{2+}$ may occur in a closed system deficient in SO_4^{2-}. However, SO_4^{2-} produced by the oxidation of pyrite or the addition of a SO_4^{2-} buffer such as gypsum could substantially reduce the amount of $^{226}Ra^{2+}$ leached. The buffering of the system with calcite may not have a major effect on the reduction of $^{226}Ra^{2+}$ leaching but if pH-buffering by calcite in a tailings basin is required for other reasons, its addition will help retard, rather than promote, the leaching of $^{226}Ra^{2+}$.

It is important to note that all of the model calculations have assumed thermodynamic equilibrium. There are significant kinetic effects controlling sulfate reduction that are not reflected in the model results.

Evidence in the literature indicates that the chemical reduction of SO_4^{2-}

to S^{2-} does not proceed at a measurable rate. Exchange reaction studies by Voge (28) in alkaline solutions at 100°C showed that sulfate does not undergo reaction with either sulfide or sulfite over times as long as a day and a half. In our view this suggests that no reaction should be expected at room temperature over a period of one week.

7.3 Conclusions

The conclusions of the geochemical modelling segment of the study are as follows:

1. Geochemical models have been developed and applied to characterize the chemical behaviour of $(Ba,Ra)SO_4$ sludge. By using the computer programs SLUDGE and PHREEQE, and traditional pe-pH diagrams, the geochemical parameters controlling the leachability of $^{226}Ra^{2+}$ from sludge were identified. **The most important variable is the redox state of the sludge-leachant system because under reducing conditions barite is not a stable mineral phase.** This result is important because no previous experimental work has studied this parameter in detail. Other parameters of importance include the initial SO_4^{2-} and Ba^{2+} concentrations, pH and ionic strength of the aqueous phase. The results of simulations designed to examine these parameters correspond, in a general way, to experimental data.

2. For oxidizing conditions in which $BaSO_{4(s)}$ is a stable phase, the $(Ba,Ra)SO_4$ component of the sludge remains sparingly soluble. The solubility of barite and, therefore, the $(Ba,Ra)SO_4$ component of the sludge, is enhanced by low concentrations of SO_4^{2-} and Ba^{2+}, high ionic strength and either very low or very high pH conditions. Even

under such conditions however, the release of $^{226}Ra^{2+}$ may be relatively small. When conditions become reducing, the entire mass of radium in the sludge can be transferred to the aqueous phase. Actual $^{226}Ra^{2+}$ levels in solution will depend on the specific activity of the sludge.

3. Results of equilibrium concentration distributions calculated by the computer program SLUDGE compare very well to those calculated by the program PHREEQE in the pH range of approximately 3 to 11, thereby providing independent verification of the codes. Outside this range, however, discrepancies occur because SLUDGE was not coded to calculate ionic strength. Other independent checks on the validity of the PHREEQE code and its data base come from the series of model trials that successfully simulated the essential features of the traditional Ba-S-O-H_2O stability diagram.

4. The PHREEQE program is a useful tool to assist in the evaluation of potential sludge disposal schemes. Through simple examples it was demonstrated how the program can model possible hydrogeochemical settings. For example, the placement of sludge in a pyrite tailings basin characterized by oxidizing conditions may be a suitable disposal scheme, particularly if the tailings are pretreated with gypsum prior to emplacement of the sludge. Because PHREEQE is a very versatile code and the thermodynamic data base can be easily modified, simulating other disposal schemes under a variety of complex conditions is possible.

8.0 MICROBIOLOGICAL EXPERIMENTS

8.1 Materials and Methods

8.1.1 Culture Methods

Sulfate-reducing bacteria were estimated using a 3-tube or 5-tube most probable number (MPN) method with modified Butlin's medium (Table 12) containing 0.0001% resazurin as a redox indicator. Each tube of 10 mL medium contained two iron nails which poise the redox potential of the medium to below -280 mV (29). These also turn black when H_2S is produced and serve as a convenient indicator of sulfate reduction. To remove O_2 from the headspace, cotton-wool plugs were placed in the screw-cap tubes above the liquid and soaked with alkaline pyrogallol immediately after inoculation (29). The numbers of sulfite- and sulfate-reducing bacteria were determined by adding 3 drops of filter sterilized 10% Na_2SO_3 solution to each tube of modified Butlin's medium just prior to inoculation. Both sets of MPN tubes were incubated at approximately 20°C for 28 days.

Total anaerobes were estimated by a 3-tube MPN method using Brain Heart Infusion broth (BHI) and 1/10 strength BHI. These were incubated at approximately 20°C for 7 days in anaerobic jars using the BBL Gaspak system. Aerobic heterotrophic bacteria were enumerated after 7 days incubation at approximately 20°C using the spread plate method on Plate Count Agar (PCA) and on 1/10 strength PCA.

Duplicate enrichment cultures for the detection of sulfur-oxidizing Thiobacillus sp. were established using 25 mL aliquots of each of the five sludge/sediment samples from the Cluff Lake site. These were inoculated into a 500 mL flask containing 25 mL of double strength medium formulated by Barton and Shively (30) using sublimed sulfur as the energy source. One flask in each duplicate set was inoculated with a culture of T. thiooxidans ATCC 8085

Table 12. Composition of Modified Butlin's Medium.

Compound[a]	Weight (g)
K_2HPO_4	0.5
NH_4Cl	1.0
Na_2SO_4	2.0
$CaCl_2 \cdot 2H_2O$	0.067
$MgSO_4 \cdot 7H_2O$	1.0
$FeSO_4 \cdot 7H_2O$	0.0036
Yeast extract	1.0
Resazurin	0.001
Sodium lactate (60% syrup)	2.5[b]

[a] All added to distilled water to make up a total volume of 1000 mL.

[b] mL

The pH of the medium was then adjusted to pH 7.5 with NaOH.

to ensure that the method could detect sulfur-oxidizing bacteria. The cultures were incubated at approximately 20°C and the change in pH was measured using narrow-range pH paper to detect sulfur oxidation.

8.1.2 Epifluorescent Microscopy

Each of the four samples collected in May 1984 from the Cluff Lake mine site were diluted to 1 in 100 or 1 in 1000, stained with acridine orange and examined by epifluorescent microscopy using the methods of Wyndham and Costerton (31).

Nalidixic acid (final concentration 0.002%) was added to Butlin's medium to inhibit cell division in attempts to enumerate living bacteria using epifluorescent miscroscopy (32). One mL aliquots of sludge from Pond A-2 (Cluff Lake) were added to several screw cap culture tubes which contained 9 mL of Butlin's medium or 9 mL of Butlin's medium in which 24 mg/mL glucose was substituted for sodium lactate. Cotton-wool plugs were placed in the headspace of the tubes and these were soaked with alkaline pyrogallol. The tubes were sealed and incubated at room temperature. After various incubation times (2 to 21 days) one tube containing each culture medium was opened and an aliquot removed for staining with acridine orange. These stained preparations were examined by epifluorescent microscopy for elongated cells.

Pure cultures of Desulfotomaculum orientis and Desulfovibrio vulgaris were also inoculated into Butlin's medium with nalidixic acid and examined microscopically after 7 days incubation at room temperature.

8.1.3 Sulfate-reduction in the Presence of Added Carbon Sources

8.1.3.1 Initial Survey

To test whether the indigenous populations would reduce sulfate, the sludges from Elliot Lake and pond A-2 from Cluff Lake were supplemented with five different organic compounds. Individual solutions of sodium lactate, glucose, sodium acetate, sodium pyruvate and glycollic acid were prepared to a final concentration of 67 mM in distilled water which contained 0.0001% resazurin. These were sterilized by autoclaving and 2 mL of a substrate solution were added to each of three sterile 18 x 150 mm screw-cap tubes which contained two 7.5 cm iron finishing nails. To each tube, 8 mL of sludge from Elliot Lake were added followed by the placement of cotton-wool plugs soaked with alkaline pyrogallol in the headspace. Control cultures were established with sterile water plus resazurin in place of the carbon substrate solution. These were incubated at approximately 20°C for 28 days. Blackening of the nails and the sludge was used as an indication of the production of H_2S.

8.1.3.2 Release of $^{226}Ra^{2+}$ from Washed $(Ba,Ra)SO_4$ Sludges

Sludge from the Elliot Lake mine and sludge from pond A-1 at Cluff Lake were used in these experiments. Since the overlying water in these sludge samples contained high concentrations of dissolved SO_4^{2-} and because it was not expected that $(Ba,Ra)SO_4$ dissolution would occur until the dissolved SO_4^{2-} was depleted from the cultures, the sludges were washed repeatedly to reduce dissolved SO_4^{2-} concentrations. Aliquots of approximately 1 L were washed in the following manner: the sludge was allowed to settle overnight and the supernatant decanted; sterile distilled water was added to make the sludge sample back to its original volume and the sample was mixed, allowed to settle overnight and the supernatant was removed. Each repetition of this procedure removed approximately 30% of the dissolved sulfate which remained after the previous wash. The Elliot Lake sludge was washed 5 times and the Cluff Lake sludge was washed 3 times.

After the final wash, each sludge sample was made up to its original volume with sterile distilled water and mixed vigorously. Aliquots were then removed for aerobic plate counts on 1/10 strength PCA, sulfate-reducing bacteria enumerations and soluble sulfate measurements. Two sets of experiments were performed with these washed sludges.

Five different series of cultures were established in the first set of experiments. The data in Table 13 summarize the differences among these series. Each of the six cultures in a series received a different concentration of lactate. The Cluff Lake cultures received 0, 300, 1500, 3000, 4000 and 6000 mg/L lactate. The Elliot Lake cultures received 0, 500, 1500, 2500, 3500 and 4000 mg/L lactate. One series with each sludge received no nitrogen or phosphorus supplementation (series 1 and 3). All of the others were given phosphate. Series 2 and 4 received NH_4NO_3 and series 5 received NH_4Cl as nitrogen sources.

The cultures were established in sterile 158 mL serum bottles. Each bottle contained 1.3 mL sterile 0.01% resazurin solution, and suitable aliquots of sterile 1.51 g/L sodium lactate, nitrogen and phosphate solutions and distilled water to give a total volume of 10 mL of liquid prior to the addition of 140 mL of vigorously mixed washed sludge. The NP solution, which contained 100 g/L NH_4NO_3 and 59 g/L phosphate (pH 7.4), was prepared as outlined in Fedorak and Westlake (33). For the cultures in series 5, a similar solution was prepared with 144 g/L NH_4Cl substituted for the NH_4NO_3. Two mL aliquots of these nitrogen and phosphorus solutions were added to the appropriate serum bottles (Table 13).

Table 13. Summary of the First Set of Cultures Established to Demonstrate the Release of $^{226}Ra^{2+}$ from $(Ba,Ra)SO_4$ Sludges by Indigenous Microorganisms.

Series No.	Source of Sludges	Phosphate Added	NH_4NO_3 Added	NH_4Cl Added	Range of Lactate Concentrations
1	Pond A-1[a]	-	-	-	0 - 6000 mg/L
2	Pond A-1	+	+	-	0 - 6000 mg/L
3	Elliot Lake	-	-	-	0 - 4000 mg/L
4	Elliot Lake	+	+	-	0 - 4000 mg/L
5	Elliot Lake	+	-	+	0 - 4000 mg/L

[a] Cluff Lake

After the addition of the sludge, each bottle was sealed with a butyl rubber serum stopper and 1.5 mL of sterile 2.5% $Na_2S \cdot 9H_2O$ injected into the bottle to hasten the onset of anaerobic conditions in the culture. These cultures were incubated at approximately 20°C for 10 weeks with occasional shaking. Gas which formed in the series 2 and 4 bottles was vented using a hypodermic needle. At the end of the incubation period, 1 mL of 2M $FeCl_2$ was added to each culture to trap any sulfide produced as FeS. The bottles were allowed to stand at 4°C overnight and then the supernatant was decanted from each culture for chemical analysis. The supernatant was filtered through a 0.45 μm Millipore filter and 2-3 mL aliquots were removed for Ba^{2+} and in some cases Ca^{2+} analyses. The remainder of the supernatant was acidified with 5 mL of concentrated HNO_3 and used for $^{226}Ra^{2+}$ analysis. The solids which remained in the bottle were analyzed for sulfide.

The sludge from Pond A-1 at the Cluff Lake mine was used for the second set of experiments in which series 1 (Table 13) was repeated with two new lactic acid concentrations included (2500 and 3500 mg/L). These cultures were incubated for 8 weeks prior to analyses for Ba^{2+}, Ca^{2+}, $^{226}Ra^{2+}$ and S^{2-}. Twelve replicate cultures containing 3000 mg/L lactic acid (with no NP supplementation) were estblished to monitor the rate of Ba^{2+} and $^{226}Ra^{2+}$ release. Individual culture bottles were sacrificed for analyses at various times over a 51 day incubation period. At selected times during the first 12 days, aliquots from the sacrificed bottles were removed for sulfate-reducing bacteria enumerations. Since previous experience with this sludge showed that it contained a large number of aerobes, no Na_2S was added as a reducing agent at the time of inoculation of the second set of $^{226}Ra^{2+}$ release experiments.

8.1.4 Chemical Analyses

The microbiological experiments required determination of $^{226}Ra^{2+}$, barium, calcium, sulfide, sulfate and lactate.

Samples for $^{226}Ra^{2+}$ analyses were obtained by removing supernatant from the tubes or bottles. This supernatant was then drawn through a 0.45 µm filter and acidified to pH < 2 with 2-5 mL of nitric acid (conc.). The samples were then made up to 130 mL with high purity deionized water (Appendix 2.1). All samples were analyzed at least twice using the procedure described in Appendix 2.1 and were retained should any re-examination be necessary.

Barium analyses were performed by atomic absorption spectrophotometry. Calcium was measured using the microtitration method of Kratochvil and Jeremy (1976). Sulfide quantitation was performed by acidification, followed by collection of the H_2S in an excess of standard $AgNO_3$ solution and back titration of the remaining Ag^+ with KCl. Details of all three methods are given in Appendices 2.4 to 2.6.

Dry solids content of sludge samples was established by the procedure described in Section 6.2.

Sulfate concentrations were determined by a turbidimetric procedure using Sulfa Ver IV Sulfate Reagent (Hach Chemical Co., Ames, Iowa). Supernatants from cultures were diluted to 50 mL to give final sulfate concentrations between 10-100 mg/L. After adding 0.5 g of reagent, the diluted sample was mixed for 30 sec and the turbidity read at 540 nm in a 1 cm light path.

Since sodium lactate is commerically available as a syrup containing approximately 60% sodium lactate, the stock feed solution used for the $^{226}Ra^{2+}$ release experiments was analyzed for lactate prior to use by the method outlined by Dawes et al. (34).

8.2 Results

8.2.1 Microbial Content of Sludge Samples

The 3-year old sludge from Elliot Lake was used to evaluate the method for the enumeration of sulfate-reducing bacteria. In a preliminary test, all of the Butlin's tubes showed the production of H_2S. Thus, the sample had not been diluted sufficiently and the best estimate for the sulfate-reducer MPN was $>2.4 \times 10^3$ organisms/mL.

To verify that the reaction was due to microbial activity, an aliquot from a positive tube was transferred to fresh medium and incubated for 14 days. This again produced a black precipitate on the nails. This procedure was repeated through 7 sequential passages and in each case the nails turned black. Finally, an aliquot from the seventh transfer was placed onto agar plates containing Butlin's medium. After incubation in an anaerobic chamber, black colonies which are characteristic of sulfate-reducing bacteria appeared. Thus sulfate-reducing bacteria were confirmed to be present in the Elliot Lake sludge. Later microbial enumerations on this sludge showed that the sulfate-reducing bacteria enumeration was 2.3×10^4/mL.

Hydrogen sulfide is generated by sulfate-reducing bacteria and by another group known as sulfite-reducing bacteria. The latter group consists of heterotrophic, facultatively anaerobic bacteria such as Proteus, Vibrio, Pseudomonas, and Salmonella which can reduce sulfite but not sulfate to H_2S (35). The sulfate-reducing bacteria can use both sulfate and sulfite as electron acceptors to produce H_2S.

The $(Ba,Ra)SO_4$ sludges and the Snake Lake sediment samples collected in May 1984 from the Cluff Lake mine were examined for both of these groups of sulfide-producing bacteria. The data in Table 14 compare the numbers of H_2S generating bacteria obtained using Butlin's medium, which contains only

Table 14. MPNs of Sulfate- and Sulfite- plus Sulfate-Reducing Bacteria in Samples taken from the Cluff Lake Mining Operation.

	MPN/mL	
Sample	Sulfate-Reducing Bacteria	Sulfite- plus Sulfate-Reducing Bacteria
Tailings Pond Effluent	9.3×10^1	4.3×10^4*
Pond A-2	4.6×10^5	7.5×10^4
Pond B-1	1.5×10^5	1.5×10^5
Snake Lake	9.3×10^4	9.3×10^4

* Number of sulfite- plus sulfate-reducing bacteria was significantly greater than number of sulfate-reducing bacteria at the 5% significance level.

sulfate, and Butlin's medium supplemented with sulfite. In only one sample - the tailings pond effluent - were statistically different MPNs observed when the data were analyzed by the method of Cochran (36). In this sample, the sulfate-reducing bacteria were less numerous than sulfite-reducing bacteria.

The addition of sulfite to the medium quickly lowers its redox potential. This hastened growth and production of H_2S in the cultures. During the early weeks of incubation, the MPNs from the sulfite plus sulfate medium were higher than in the medium which contained only sulfate. However, by the end of the four week incubation period, the MPNs observed using the two different media were indistinguishable in three of the four samples (Table 14). Thus, the majority of the H_2S-producing organisms in Ponds A-2 and B-1, and in Snake Lake were sulfate-reducing bacteria. There were approximately 10^5/mL of these organisms in the latter three samples (Table 14).

The nutrient status in the sludge samples collected during this study was expected to be low. Therefore it was likely that the nutrient concentrations in media used for enumeration of heterotrophic bacteria influenced the viable counts observed. This was tested using full strength and 1/10 strength PCA for aerobic counts and full strength and 1/10 strength BHI for anaerobic MPNs.

The data in Table 15 summarize the number of aerobic and anaerobic bacteria in four samples collected in May 1984 from the Cluff Lake operation. These data also show that the aerobic counts obtained on 1/10 strength PCA were higher than those obtained on full strength PCA. Therefore, the dilute medium is better suited for enumerating aerobic, heterotrophic bacteria in these samples. The strength of the BHI medium did not affect the total numbers of anaerobes detected by the MPN method.

Table 15. Comparison of Microbial Counts on Samples from the Cluff Lake Mine Obtained with Full Strength and Diluted Media.

	Aerobic Count (organisms/mL)		Anaerobic Count (MPN/mL)[a]	
Sample	PCA	1/10 stength PCA	BHI	1/10 strength BHI
Tailings Pond Effluent	1×10^6	5.2×10^6*	4.3×10^6	1.5×10^7
Pond A-2	2×10^7	5.5×10^7*	2.4×10^7	9.3×10^6
Pond B-1	6.2×10^6	3×10^7*	1.1×10^8	4.6×10^7
Snake Lake	6.9×10^5	5×10^6*	7.5×10^6	4.6×10^7

[a] The MPNs obtained using BHI were not significantly different from those obtained using 1/10 strength BHI, at the 5% significance level.

* Significantly greater than counts obtained using full strength PCA, at the 5% significance level.

Thiobacillus spp. can oxidize reduced sulfur compounds, such as sulfides, elemental sulfur and thiosulfate, to sulfate. This activity can reduce $^{226}Ra^{2+}$ release as shown by Silver and Ritcey (19). This oxidation produces H_2SO_4 which causes the pH of the growth medium to drop. Thus the method for detection of the sulfur-oxidizing bacteria involves monitoring the pH changes of the medium.

All five samples from the Cluff Lake mining operation were screened for the presence of *Thiobacillus* spp. The data in Table 16 summarize the pH changes observed in the *Thiobacillus* enrichment medium over a 21 day incubation period. *T. thiooxidans* strain ATCC 8085 was inoculated into accompanying flasks to verify the detection method. The pure ATCC 8085 culture was at pH 2 after inoculation and the medium dropped to pH 0.8 after 21 days (Table 16). The pH of those cultures which were inoculated with a sludge sample and ATCC 8085 also decreased, showing that the culture method could detect the presence of *Thiobacillus* spp. The pH values also decreased in cultures inoculated with only a sludge sample (Table 16), suggesting that *Thiobacillus* spp. were present in these samples. The variations in the final pH values were probably due to the different buffering capacities of the samples, which comprised 50% of the total volume of the culture.

Five mL aliquots from each of the enrichment cultures (Table 16) were transferred to 50 mL of fresh medium to verify the presence of the sulfur-oxidizing *Thiobacillus* spp. After these had incubated for 21 to 28 days a second sequential transfer was made. After a further 3 to 4 weeks incubation, the final pH values in all of the second sequential cultures were > 2. Therefore we conclude that *Thiobacillus* spp. were present in all five samples from the Cluff Lake mine.

Table 16. pH Changes in Thiobacillus Enrichment Cultures During a 21 Day Incubation Period[a] in Samples Collected from the Cluff Lake Mining Operation.

Culture	Day 0	Day 14	Day 21
Thiobacillus thiooxidans ATCC 8085	2	1	0.8
Tailings pond effluent	4.5	3.5	3.5
Tailings pond effluent + ATCC 8085	2	1	1
Pond A-1	6	4	4
Pond A-1 + ATCC 8085	6	3.7	3.5
Pond A-2	6	5.5	5.2
Pond A-2 + ATCC 8085	6	5.5	4.5
Pond B-1	5	3.5	3
Pond B-1 + ATCC 8085	4	2.5	2.5
Snake Lake	4.5	2	1.5
Snake Lake + ATCC 8085	2.5	1.5	1

[a] Medium adjusted to pH 4 prior to inoculation.

The data in Table 17 summarize the results of the enumeration and detection of various viable bacterial groups in all of the sludge and sediment samples examined throughout this study. Sulfate-reducing bacteria were present in all of the $(Ba,Ra)SO_4$ sludges examined. The aerobic and anaerobic counts in the Cluff Lake mine wastewater streams were similar to those in the Snake Lake sediment.

The results in Table 17 also show that active heterotrophic populations were present in these aquatic environments and therefore transformations of organic compounds would be likely to occur within these waters. The combination of heterotrophic bacteria and sulfate-reducing bacteria in the secondary treatment ponds A-1, A-2 and B-1 suggest that active sulfate-reduction may be occurring in the Cluff Lake ponds. During a 1984 cleaning of pond A-1 workers at the Cluff Lake mine found black sludge at the bottom of the pond and could smell H_2S. It is very likely that these sulfides were produced by microbial activity.

8.2.2 Epifluorescent Microscopy

The abundance of particulate matter in the sludge samples made microscopic counting of bacteria very difficult. To overcome these problems, each of four Cluff Lake samples collected in May 1984 was diluted to 1 in 100 or 1 in 1000 to enable examination by epifluorescent microscopy. Total cell counts were made and these results are compared in Table 18 to the total viable aerobic plate counts. The epifluorescent microscopic method gives an estimate of the total number of bacterial cells present - whether they are viable or dead. In contrast, the plate count method estimates only the number of viable cells that can grow under the culture conditions used. Thus the epifluorescence method would be expected to give higher results than the plate

Table 17. Summary of Viable Bacteria Detected in Samples Investigated During this Project.

Sample	Sulfate-reducers (MPN/mL)	Aerobic Count[a] (organism/mL)	Anaerobic Count[b] (MPN/mL)	*Thiobacillus* spp Present
$(Ba,Ra)SO_4$ sludge from Elliot Lake mine	2.3×10^4	1×10^6	ND[c]	ND
Tailings pond effluent from Cluff Lake mine	9.3×10^1	5.2×10^6	1.5×10^7	Yes
$(Ba,Ra)SO_4$ sludges from Cluff Lake mine				
Pond A-1	1.7×10^6	1.8×10^7	ND	Yes
Pond A-2	4.6×10^5	5.5×10^7	9.3×10^6	Yes
Pond B-1	1.5×10^5	3×10^7	4.6×10^7	Yes
Snake Lake sediment from Cluff Lake mine	9.3×10^4	5×10^6	4.6×10^7	Yes

[a] Determined on 1/10 strength PCA

[b] Determined on 1/10 strength BHI

[c] Not Determined

count. Such results are seen in Table 18.

A method which incorporates nalidixic acid into the growth medium was also used to examine the viability of the microorganisms. The method is based on the fact that nalidixic acid interferes with the cellular division of many bacteria. In actively growing cultures, this results in the formation of long individual cells rather than many normal size cells. These can be stained and examined by epifluorescent microscopy as an estimation of the viability of a microbial population. This technique was applied to aliquots of the A-2 sludge from the Cluff Lake mine. Lactate and glucose were used individually as carbon sources in cultures grown under anaerobic conditions. Some elongated cells were observed but in general the method was unsuccessful. Pure cultures of two species of sulfate-reducing bacteria (*Desulfotomaculum orientis* and *Desulfovibrio vulgaris*) were grown in Butlin's medium with nalidixic acid and examined microscopically. The elongated cells were very evident in the *D. orientis* culture but much less so in the *D. vulgaris* culture.

Further use of epifluorescent microscopy was not pursued since it had been initially proposed as an alternative means to demonstrate viable bacteria in the sludges which were expected to have relatively low microbial densities.However, other culture methods readily demonstrated the presence of various types of bacteria including aerobes, anaerobes, sulfate-reducing bacteria and sulfur-oxidizing bacteria (Table 17). Therefore the nalidixic acid culture method and the subsequent laborious epifluorescent microscopic enumeration were not continued.

Table 18. Microbial Cell Counts in Cluff Lake Samples Collected in May 1984.

Sample	Total Viable Aerobic Count/mL[a]	Epifluorescence Count/mL
Tailings Pond Effluent	5.2×10^6	2.3×10^7
Pond A-2	5.5×10^7	8.2×10^8
Pond B-1	3×10^7	4.4×10^7
Snake Lake	5×10^6	4.0×10^7

[a] Counts done on 1/10 strength PCA.

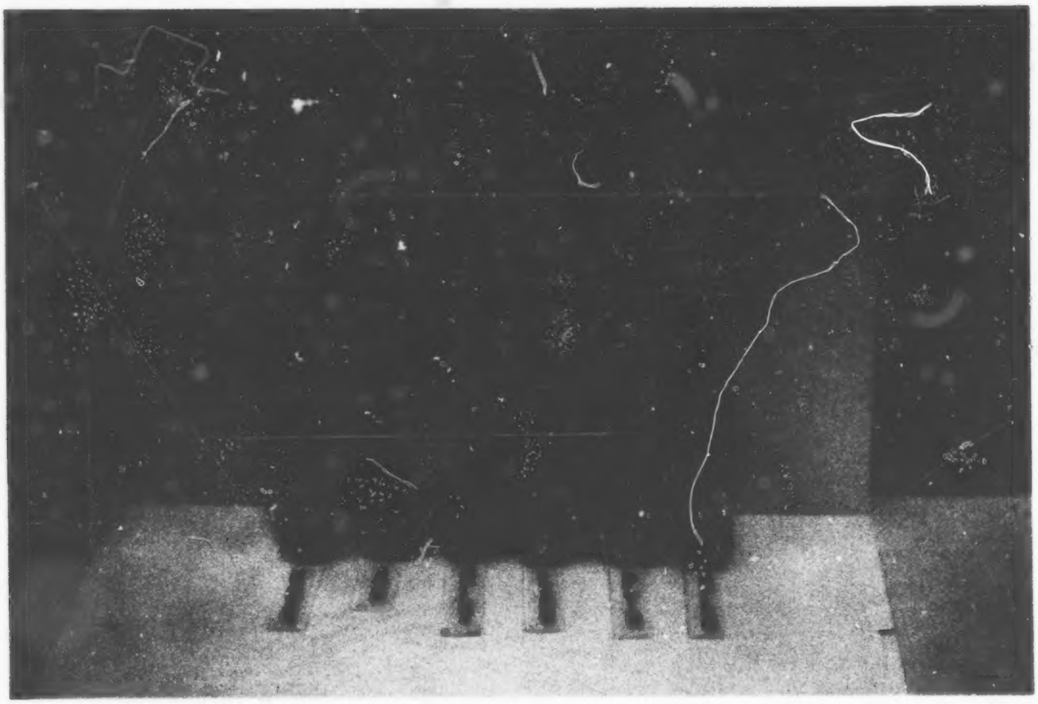
8.2.3 Sulfate-reduction in the Presence of Added Carbon Sources

The most well known genera of sulfate-reducing bacteria are *Desulfovibrio* and *Desulfotomaculum*. Most species in these genera can use lactate and pyruvate as carbon and energy sources with sulfate serving as their terminal electron acceptor (37). Only one species in each genus will grow on acetate but not lactate and pyruvate. One species of *Desulfovibrio* and two species of *Desulfotomaculum* will grow on glucose. Several new genera of sulfate-reducing bacteria have been recently described (37, 38). Lactate, pyruvate and acetate serve as carbon and energy sources for most of the new species.

8.2.3.1 Initial Survey

The Elliot Lake sludge was first used to determine whether sulfate-reduction could be stimulated by the addition of various carbon and energy sources. Lactate, pyruvate and acetate were used as test substrates. Glycollic acid was also evaluated because it is a product of photosynthesis and is often excreted by freshwater algae (39). Glucose is seldom used by sulfate-reducing bacteria; however, fermentation products resulting from the activity of anaerobes in the sludge would provide suitable substrates for sulfate reduction.

Figure 8 shows the sludge-containing tubes which received various carbon sources after 28 days incubation. In all six cultures including the control the nails blackened from H_2S production. The sludge in those cultures which received added carbon sources also blackened - presumably due to the presence of iron in the sludge (Table 7). The acetate-supplemented culture produced the least amount of H_2S and discrete black particles were observed in the sludge. With glycollate or lactate present, nearly all of the sludge was



* CON = control, no substrate added: AC = acetate; GLY = glycollate; LAC = lactate; PYR = pyruvate; GLU = glucose.

Figure 8. The Effects of Added Carbon Sources on Sulfate Reduction in Sludge from Elliot Lake.
Blackening indicates H_2S production.

black. These results clearly show that the addition of suitable carbon compounds can increase the activity of the sulfate-reducing bacteria present in the $(Ba,Ra)SO_4$ sludge. The production of H_2S from glucose supplementation suggests the presence of microorganisms which can ferment this carbohydrate to compounds that can be used by sulfate-reducing bacteria.

Aliquots of the sludge from pond A-2 at Cluff Lake were also supplemented with each of the following substrates: acetate, glycollate, lactate, pyruvate or glucose. In each case, the added substrate resulted in the production of sulfide as indicated by the formation of a black precipitate in the sludge. Except for the case of acetate, the iron nails in the culture tubes also blackened. These results were similar to those observed with the Elliot Lake sludge (Figure 8) and indicated that if an appropriate carbon source were available to the microorganisms in these sludges, sulfate-reduction would occur.

8.2.3.2 Release of $^{226}Ra^{2+}$ from Washed $(Ba,Ra)SO_4$ Sludges

The data in Table 19 show the effects of washing the two sludges with sterile distilled water. The purpose of the washes was to reduce the amount of soluble sulfate in the sludge added to the culture bottles. Three washes of the sludge from the Cluff Lake mine reduced the sulfate concentration from 630 to 160 mg/L and five washes of the Elliot Lake sludge reduced the sulfate concentration from 1240 to 270 mg/L. The washes had little effect on the numbers of microorganisms in the sludge. This suggests that a large portion of the population was attached to the sludge particles and could not be removed by these washes. Thus, there were large numbers of indigenous aerobes and sulfate-reducing bacteria in the washed sludge inocula used to determine whether $^{226}Ra^{2+}$ could be released in the presence of lactate.

Table 19. Characteristics of the $(Ba,Ra)SO_4$ Sludges Used for the First Set of $^{226}Ra^{2+}$ Release Experiments.

Sludge Sample	Number of Washes	Soluble Sulfate in Supernatant (mg/L)	Aerobic Microbial Count (organisms/mL)	Sulfate-Reducing Bacteria (MPN/mL)
Cluff Lake (Pond A-1)	0	630	1.8×10^7	1.7×10^6
	3	160	2.4×10^6	4.3×10^5
Elliot Lake	0	1240	1×10^6	2.3×10^4
	5	270	1.1×10^6	9.3×10^4

The amounts of sulfide produced in 10 week old cultures and the concentrations of Ba^{2+} and $^{226}Ra^{2+}$ in the supernatants of Series 1 and 3 are shown in Figures 8 and 9 respectively. In both cases, soluble Ba^{2+} and substantial amounts of $^{226}Ra^{2+}$ were released when a suitable carbon and energy source was available for the sulfate-reducing bacteria. In Series 1, Ba^{2+} concentrations up to 148 mg/L and $^{226}Ra^{2+}$ activity of 130 Bq/L were released from the Cluff Lake sludge (Figure 9). In Series 3, Ba^{2+} concentrations reached 244 mg/L and the $^{226}Ra^{2+}$ activity reached 426 Bq/L (Figure 10). Both figures show strong correlations between the amount of sulfide produced and the concentrations of Ba^{2+} and the activities of $^{226}Ra^{2+}$ present in the culture supernatants. The solubilization of these two cations generally increased with increased initial lactate concentrations in Series 3 (Figure 10). This was expected since the more lactate present, the more potential there was for sulfate-reduction. The data in Figure 6 show a maximum concentration of Ba^{2+} and $^{226}Ra^{2+}$ at an intermediate lactate concentration of 3,000 mg/L. The same trend was also observed in a later experiment (Figure 11).

The results in Figures 9 and 10 clearly show that the indigenous sulfate-reducing populations in these two sludges can liberate $^{226}Ra^{2+}$ if adequate supplies of a suitable carbon and energy source are available. Without lactate supplementation, there was virtually no $^{226}Ra^{2+}$ in the culture

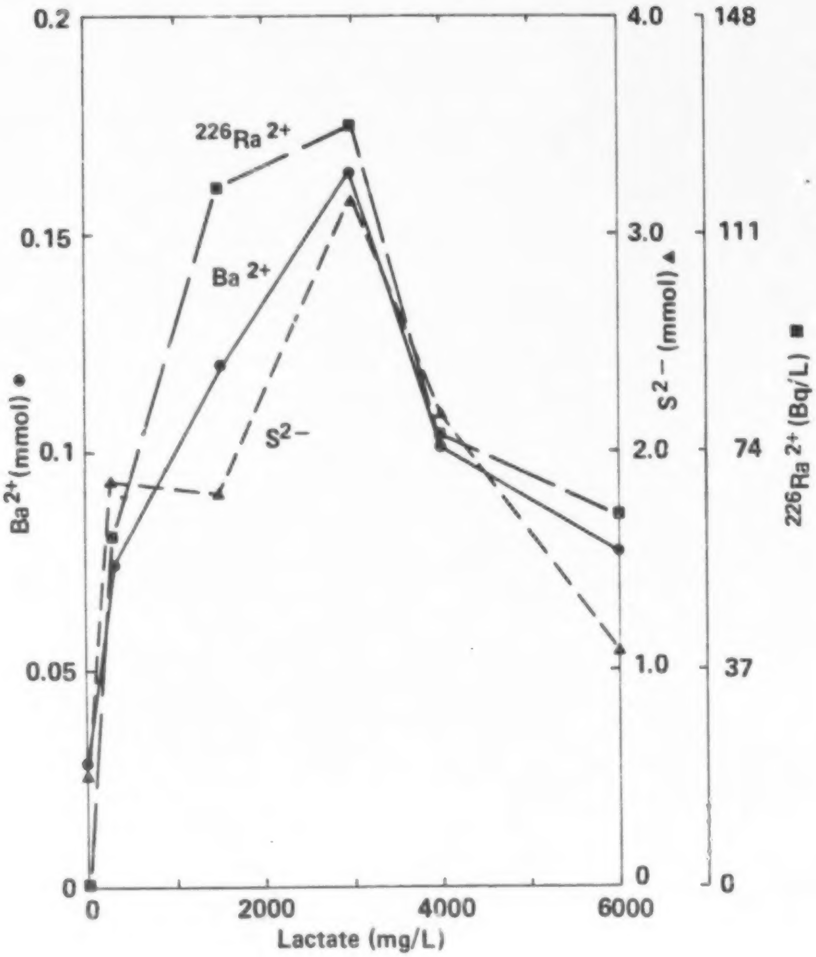


Figure 9. The Production of Sulfide and the Release of Ba^{2+} and ^{226}Ra^{2+} from Washed Sludge from Pond A-1 at the Cluff Lake Mine (series 1).

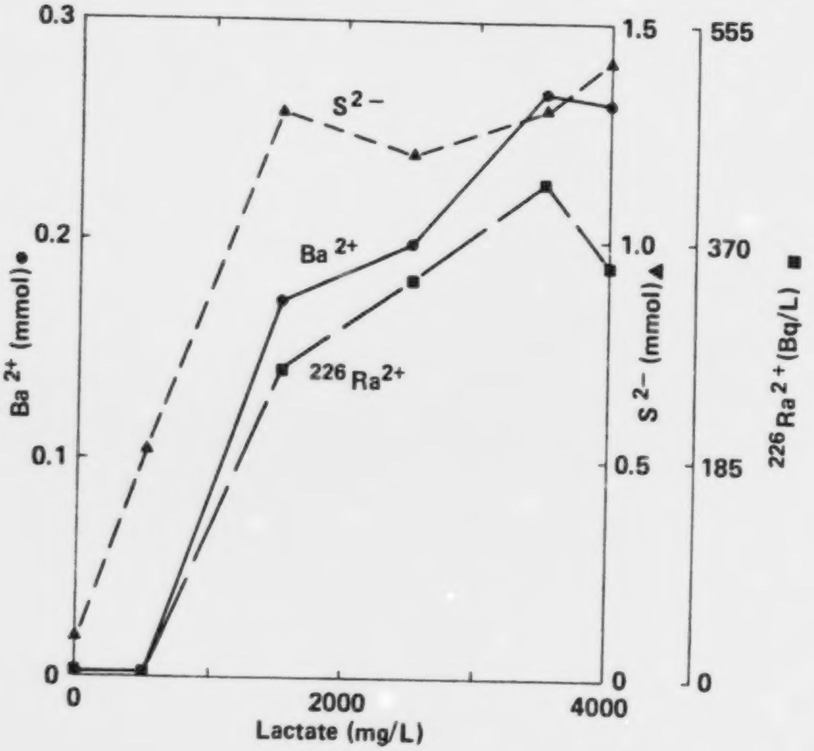


Figure 10. The Production of Sulfide and Release of Ba^{2+} and $^{226}Ra^{2+}$ from Washed Sludge from the Elliot Lake Mine (series 3).

supernatants: in the 0 mg/L lactate cultures the $^{226}Ra^{2+}$ activity was 0.37 Bq/L with the Cluff Lake sludge (Figure 9) and 0.19 Bq/L with the Elliot Lake sludge (Figure 10). Thus, while the actual $^{226}Ra^{2+}$ activity levels in solution were specific to these experimental conditions, the presence of a suitable carbon source was able to increase $^{226}Ra^{2+}$ release by up to 4 orders of magnitude.

Phosphate and various forms of fixed nitrogen were added to the series 2, 4 and 5 cultures (Table 13) to ensure that these nutrients were not limiting in the batch cultures. The results in Table 20 compare the concentrations of Ba^{2+} and $^{226}Ra^{2+}$ liberated in cultures with and without NP supplementation. In each case analyses were done on the supernatants from the cultures with the highest lactate doses.

A comparison of Ba^{2+} and $^{226}Ra^{2+}$ release in series 1 and series 2 (Table 20) shows that there was less dissolution in the latter series which had been supplemented with NH_4NO_3 and P. This trend was also observed in the series 3 and series 4 cultures. This difference likely occurred because nitrate, like sulfate, also serves as a terminal electron acceptor for certain bacteria, but not sulfate-reducing bacteria. These nitrate-reducing bacteria grow more quickly than sulfate-reducing bacteria and therefore out-compete the latter group for nutrients (lactate in these experiments). Thus less lactate would be available for the sulfate-reducing bacteria and less $(Ba,Ra)SO_4$ sludge would be dissolved.

The microbial process of nitrate reduction is known as denitrification and the metabolic endproducts include gases such as N_2, N_2O and NO. Vigorous gas production was observed in many of the series 2 and series 4 cultures. Although not measured, gas production appeared to be higher (i.e. higher total pressure) in the cultures which initially contained higher lactate

Table 20. Comparison of Ba^{2+} and $^{226}Ra^{2+}$ Release from Cultures with and without N and P Supplementation (at highest lactate doses).

Culture Treatment	Series No.	Initial Lactate Concentration (mg/L)	Ba^{2+} (mmole)	$^{226}Ra^{2+}$ (Bq/L)
Cluff Lake				
without NP	1	6000	0.077	62.5
with NH_4NO_3 + P	2	6000	0.044	26.6
Elliot Lake Sludge				
without NP	3	4000	0.26	343
with NH_4NO_3 + P	4	4000	0.007	10.7
with NH_4Cl + P	5	4000	0.05	31.5

concentrations. Those cultures which contained no added lactate or only low doses produced very little gas. These observations are consistent with the ability of nitrate-reducing bacteria to out-compete sulfate-reducing bacteria for nutrients.

The cultures with the Elliot Lake sludge supplemented with NH_4Cl and phosphate (series 5) released more Ba^{2+} and $^{226}Ra^{2+}$ than the series 4 cultures which contained NH_4NO_3, but much less than the unsupplemented series 3 cultures (Table 20). The reason for this relatively low release is not clear since the addition of NH_4^+ as a nitrogen source for the sulfate-reducing bacteria would be expected to enhance the release of divalent cations from the sludge. Further investigations to explain these observations were beyond the scope of the present project and therefore no other experiments with NH_4^+ supplemented cultures were conducted. However, this set of experiments clearly shows that if the indigenous populations in washed (i.e. soluble sulfate depleted) sludges are supplied with a suitable carbon and energy source, sulfide production occurs with the concurrent release of $^{226}Ra^{2+}$. The experiments also show that the sludges contain adequate amounts of N and P for these microbial activities.

Washed sludge from pond A-1 at the Cluff Lake mine was used for a second set of $^{226}Ra^{2+}$ release experiments. After washing, this sludge contained 200 mg/L sulfate and 3.3×10^5 sulfate-reducing bacteria/mL. The series 1 experiment was repeated and the results of the chemical analyses of the cultures after 8 week incubation are shown in Figures 11 and 12. Enough sulfide (0.708 mmol) was present in the culture which received no added lactate to give the sludge a black colour. The 300 mg/L lactate dose provided 0.5 mmol of this substrate to the culture. Since sulfate-reducing bacteria require 2 mol of lactate to reduce 1 mol of SO_4^{2-} (37), the amount of

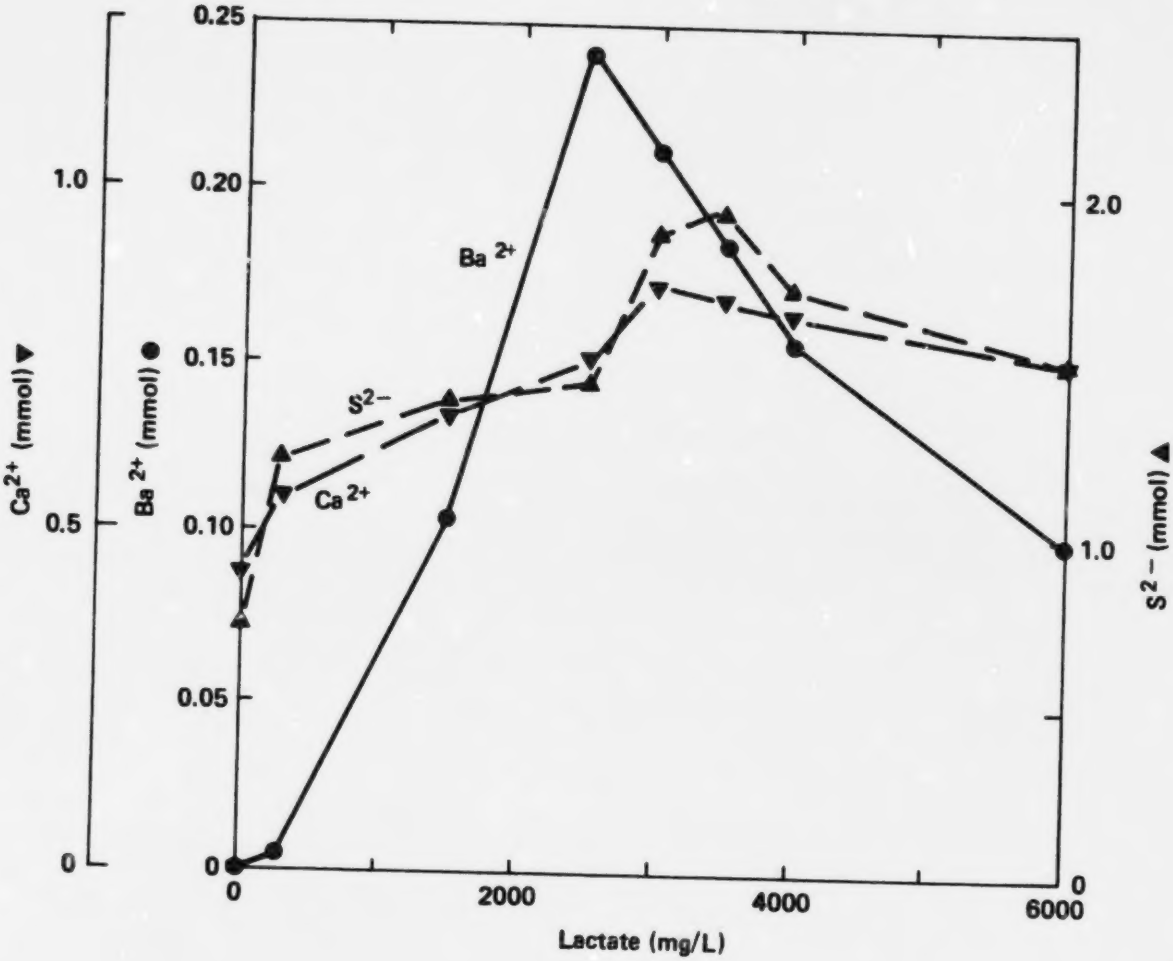


Figure 11. The Production of Sulfide and the Release of Ba^{2+} and Ca^{2+} from Washed Sludge from Pond A1 at the Cluff Lake Mine

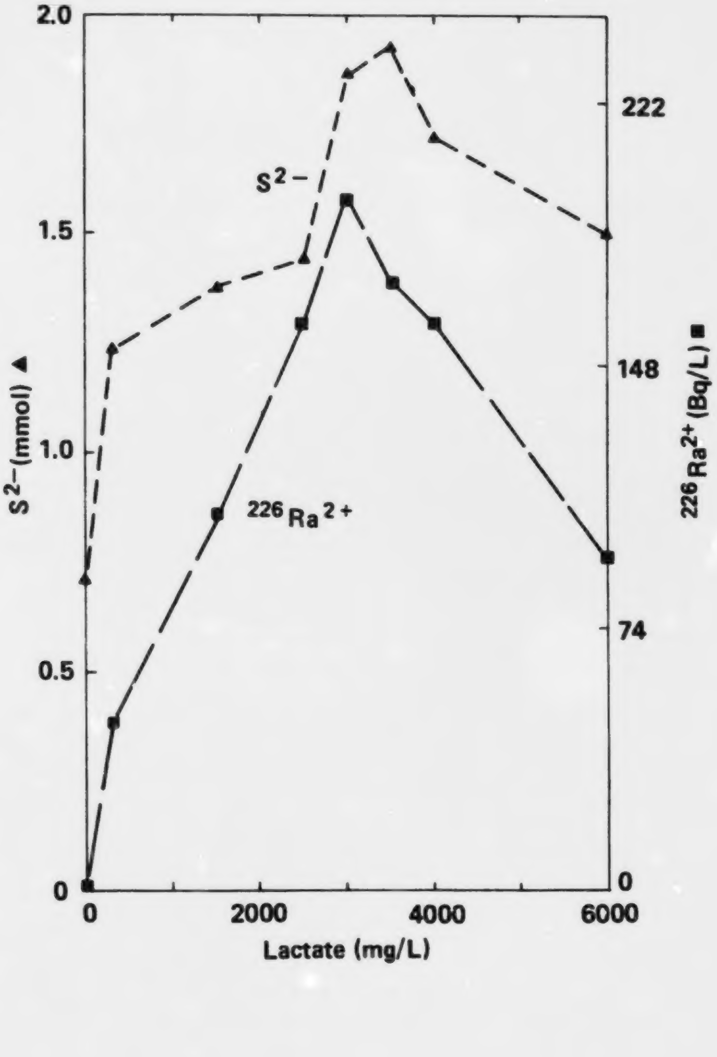


Figure 12. The Production of Sulfide and the Release of $^{226}Ra^{2+}$ from Washed Sludge from Pond A-1 at the Cluff Lake Mine.

substrate in this culture should cause the reduction of 0.25 mmol of SO_4^{2-}. After the sludge washing procedure, the culture was left with a total of 0.29 mmol SO_4^{2-}. Thus the majority of the soluble SO_4^{2-} should be reduced in the 300 mg/L lactate culture with little dissolution of the $(Ba,Ra)SO_4$ and therefore little release of Ba^{2+} or $^{226}Ra^{2+}$. The data in Figures 11 and 12 show that there was very little Ba^{2+} or $^{226}Ra^{2+}$ in the supernatant of the culture which received 300 mg/L lactate. As expected, higher lactate doses caused dissolution of the $(Ba,Ra)SO_4$ in the sludge with concurrent release of Ba^{2+} and $^{226}Ra^{2+}$. Since the sludge also contained $CaSO_4$ (Table 7), the sulfate reduction also released Ca^{2+} as shown in Figure 8.

In agreement with the results from the series 1 experiment (Figure 9), a maximum S^{2-} production and Ba^{2+} and $^{226}Ra^{2+}$ release occurred at lactate doses between 2500 and 4000 mg/L (Figures 11 and 12 respectively). These observations may be artifacts of the batch culture methods and the 8 and 10 week incubation times.

The data in Figure 13 show the results of the rate experiment in which the supernatants from cultures supplemented with 3000 mg/L lactate were analyzed for Ba^{2+} and $^{226}Ra^{2+}$. After a 2-day lag period there was a rapid release of these cations. By day 5 approximately 1/4 of the total observed Ba^{2+} and $^{226}Ra^{2+}$ release had occurred. Between day 5 and the final sampling time (day 56), the release of these cations was linear. The rate of Ba^{2+} release was 3.0 μmol/day ($r = 0.986$) and the rate of $^{226}Ra^{2+}$ release was 2.48 Bq/L/day ($r = 0.957$). Since the rates had not decreased by day 56, it is likely that the 3000 mg/L lactate had not been depleted by that time. McCready and Krouse (22) suggest that the rate of bacterial sulfate-reduction is limited by the solubilization rate of $BaSO_4$. Therefore if cultures had been incubated longer, the amounts of Ba^{++} and $^{226}Ra^{2+}$

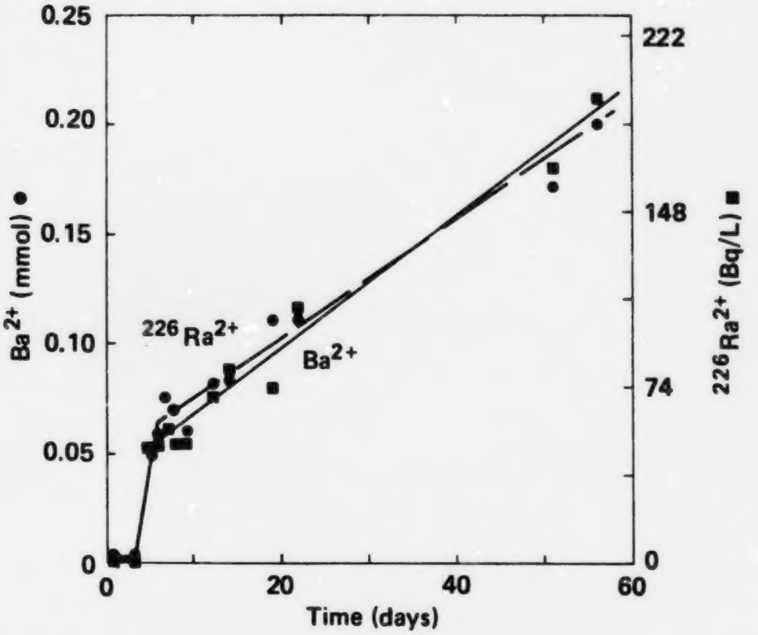


Figure 13. Rate of Release of Ba^{2+} and $^{226}Ra^{2+}$ from Washed Sludge from Pond A-1 at the Cluff Lake Mine.

released may have been higher.

It appears that the rates of release of these cations were lower at lactate concentrations of 4000 and 6000 mg/L since their final concentrations after 8 weeks incubation (Ba^{2+} in Figure 11 and $^{226}Ra^{2+}$ in Figure 12) were lower than observed in the 3000 mg/L culture. In those cultures which received high lactate doses, it is unlikely that this substrate is rate limiting and the amounts of Ba^{2+} and $^{226}Ra^{2+}$ released may have increased if the cultures had been incubated longer. However, there are several factors which complicate this prediction. Postgate (40) reports that sulfide, which accumulates in batch cultures of sulfate-reducing bacteria, acts as a growth inhibitor. Also, sulfide precipitates iron, which is required as a micronutrient for sulfate-reducers, so that iron rather than the carbon and energy source may become limiting. McCready and Krouse (22) point out that the observed amounts of Ba^{2+} may be lower than the actual amounts released since sulfate-reducing bacteria also produce CO_2, which precipitates $BaCO_3$.

The numbers of sulfate-reducing bacteria as determined during the first 12 days of the rate experiment are summarized in Table 21. On two occasions (days 5 and 9) the MPNs were significantly greater than the initial count at day zero. However, no consistent increase in MPNs was observed. Thus, an increase in the numbers of sulfate-reducing bacteria could not be detected during the time of rapid Ba^{2+} and $^{226}Ra^{2+}$ release. These results demonstrate that bacteria can be metabolically very active and cause changes to their environment without increasing the population size.

Table 21. Sulfate-Reducing Bacteria Enumerations during the First 12 Days of the Rate Experiment

Incubation Time (days)	Sulfate-reducing Bacteria (MPN/mL)
0	3.3×10^7
2	1.7×10^8
5	7.0×10^8*
7	1.7×10^8
9	9.3×10^8*
12	7.9×10^7

* Significantly greater than the counts at time zero, at the 5% significance level.

8.3 Conclusions

The results of the microbiological studies with two (Ba,Ra)SO_4 sludges have shown that if environmental conditions are suitable, microbially mediated release of $^{226}Ra^{2+}$ can occur. The microbial populations in the sludges included aerobes, anaerobes, sulfur-oxidizing, denitrifying and sulfate-reducing bacteria. When an adequate supply of carbon and energy is provided to anaerobic sludge, sulfate-reduction yields sulfide with concurrent release of $^{226}Ra^{2+}$ from the (Ba,Ra)SO_4. Since this release occurs relatively quickly, the bacteria act as catalysts. The dissolution of the sludge predicted by the geochemical modelling is thus effected much more rapidly than in a purely chemical system.

To minimize the potential for $^{226}Ra^{2+}$ release from these sludges, the following precautions should be taken in selecting disposal sites:

1. The oxygen tension and/or redox potential of the sludge should be maintained high enough to inhibit sulfate-reduction. Since sulfate-reducing bacteria are strict anaerobes, they are not metabolically active under aerobic conditions. Also, in the presence of other terminal electron acceptors such as O_2 or nitrate, the sulfate-reducing bacteria cannot successfully compete for available carbon sources and sulfate-reduction does not occur under these conditions.
2. The contamination of the sludges with organic compounds should be avoided. Although the sulfate-reducing bacteria can only metabolize a narrow range of organic substrates, the activities of other heterotrophic bacteria present in the sludge would likely transform the more complex organics into compounds which are suitable carbon and energy sources for the sulfate-reducing bacteria.

3. The liquid contacting the sludge should contain adequate concentrations of soluble sulfate. This will ensure that if sulfate-reduction does occur, the presence of excess sulfate ion will keep the $^{226}Ra^{2+}$ precipitated as $(Ba,Ra)SO_4$.

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LEACHABILITY OF RADIUM-226 FROM BARIUM-RADIUM SULPHATE SLUDGES

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APPENDICES

A Report Prepared For:

The National Uranium Tailings Program
Canada Centre for Mineral and Energy Technology
Energy, Mines and Resources Canada
Ottawa, Ontario
K1A 0G1

by

Dr. P. M. Huck
Department of Civil Engineering
University of Alberta
Edmonton, Alberta

186 pp

APPENDIX 1

Bibliography of Literature on Radium in Uranium Mine Tailings and its Removal by Coprecipitation with Barium Sulfate

Bibliography of Literature on Radium in Uranium Mine Tailings and Its Removal by Coprecipitation with Barium Sulfate

Norine Motkosky and Byron Kratochvil

March 1985

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APPENDIX 2

ANALYTICAL METHODS

APPENDIX 2.1

RADIUM-226 ANALYSIS PROCEDURE

Following sample preparation, 130 mL of the sample whose radium-226 content is to be determined is poured into a radon bubbler tube. The bubbler tube is then placed on the degassing unit and de-emanated for 3 minutes to purge any radon-222 which may be associated with the sample. When the purge is complete the bubbler tube is sealed and stored for a minimum of 6 days with most samples averaging 7 to 10 days for the in-growth of radon-222.

Once the in-growth period is complete the bubbler tube is again placed on the degassing unit and a 3 minute de-emanation draws any radon in solution into a scintillation cell.

All scintillation cell backgrounds are determined by counting overnight for a period of 16 to 17 hours immediately prior to radon collection.

Once the de-emanation is complete the cell is removed and inserted into the photomultiplier tube chamber within the radon detector unit. The cell is then allowed to sit for a minimum of 4 hours to facilitiate the equilibrium of the alpha counting rate of radon and decay products. The sample is then counted for 2 to 3 hours and a count is obtained, which when related to similarly treated radium standards yields the radium-226 activity level of the sample. All calculations are as outlined in Standard Methods for the Examination of Water and Wastewater, 1980.

Following counting of the sample the scintillation cell is flushed by evacuating 3 to 6 times and then allowed to sit for approximately 10 days before reuse. Analytical capability as per this procedure is 15 samples per week.

NBS STANDARD

In late January 1985 new cell calibration constants were determined using a standard radium-226 solution obtained from the National Bureau of Standards in Gaitherburg, MD, U.S.A. The solution contained 369.260 pCi of $^{226}Ra^{2+}$ activity, following correction for decay of radium since the time of preparation on April 1, 1984. This solution was diluted to 1,000 mL with an acid barium chloride solution and five 130 mL volumes were removed and placed into separate de-emanation (bubbler) tubes to determine cell calibration constants for each of the three radon detectors we have on hand. Each bubbler tube contained 48.004 pCi of radium-226 activity.

National Uranium Tailings Program - Standard B (Solid)

$^{226}Ra^{2+}$ Activity Level Determination

Sample preparation

The (Ba,Ra)SO_4 solid standard was desiccated overnight at room temperature. Four samples were then removed and placed into preweighed aluminum weighing dishes and weighed. Each sample was the ntransferred to a 250 mL beaker which contained a 0.1 M solution of EDTA (disodium salt) adjusted to pH 10.0 with NaOH. The solution was then heated to approximately 90°C and stirred for approximately one hour on a magnetic stirrer. This resulted in complete dissolution of the solid in the EDTA.

The solution was then made up to the required 130 mL volume with deionized water and analysed for $^{226}Ra^{2+}$ using the radon de-emanation method (as described in the interim report).

Dry weight of (Ba,Ra)SO_4 precipitate in each sample

Sample Number	Dry weight (g)
1	0.20667
2	0.24019
3	0.43621
4	0.29752

An activity level range for the determination of $^{226}Ra^{2+}$ was not provided nor were any details on solid composition. The only element analyzed for was $^{226}Ra^{2+}$ as analysis for other elements was not requested.

SASKATCHEWAN RESEARCH COUNCIL

REPORT OF CHEMICAL ANALYSIS

NOV 29 '84

Sample: 1 solid sample (Ba,Ra-SO4 solid standard material from Canmet)

Source: University of Alberta
Department of Civil Engineering
EDMONTON, Alberta T6G 2G7 Attention: W.B. Anderson

SRC Group No.: 84-1691 Purchase Order No.:

ANALYTE	UNITS	SRC LAB#11613
Ra-226		
Emanation Method	pCi/g	102
Gamma Spectroscopy	pCi/g	99

Received: Nov.20/84
Started: Nov.20/84
Completed: Nov.28/84

Analysts: L.MacDonald/G.Smithson

U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate

Standard Reference Material 4950E

Radioactivity Standard

Radionuclide	Radium-226 (1)*
Source identification	4950E
Source description	Liquid in 5-ml borosilicate-glass ampoule
Solution composition	1.9 mg of barium chloride per gram of 1.4 molar hydrochloric acid (2,3)
Mass	4.9314 ± 0.0076 grams (4)
Radium-226 concentration	7.566×10^{-11} grams of ^{226}Ra per gram of solution (5)
Reference time	April 1, 1984
Random uncertainty	0.11 percent (6)
Systematic uncertainty	1.19 percent (7)
Total uncertainty (Random plus systematic)	1.30 percent
Photon-emitting impurities	None observed (8)
Half life	1600 ± 7 years (9)
Measuring instrument	NBS pressurized "4π"γ ionization chamber calibrated with the national radium standards

This Standard Reference Material was prepared in the Center for Radiation Research, Nuclear Radiation Division, Radioactivity Group, Dale D. Hoppes, Group Leader.

Gaithersburg, MD 20899
May 1984

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

NOTES

(1) This standard was prepared by a gravimetric dilution of ^{226}Ra SRM 4953D.

(2) Solution density is approximately 1.02 at 22°C.

(3) Samples of the $BaCl_2$ used to prepare the carrier solution were measured in a NaI(Tl) well crystal and found to contain 2.5×10^{-13} g of ^{226}Ra per gram of $BaCl_2$. The ratio of the ^{226}Ra in the $BaCl_2$ to that in this standard is 6.2×10^{-6}.

(4) The uncertainty is one half the 99-percent confidence interval of the mean of 12 individually weighed masses of solution from which the average mass was calculated.

(5) The corresponding activity concentration is 2.767 Bq (7.479×10^{-11} Ci) ^{226}Ra per gram of solution.

(6) Half the 99-percent confidence interval of the mean (2.947 times the standard deviation of the mean computed from 16 ionization-chamber measurements).

(7) Linear sum of the estimated upper limits of uncertainties due to:

a) ionization chamber calibration	0.81 percent
b) half-life correction	0.13 percent
c) gravimetric measurements	0.25 percent

(8) The limits of detection for impurity photons as a percentage of the emission rate of the 609-keV gamma ray from ^{226}Ra is 0.1 percent between 90 and 1900 keV, provided that the impurity photons are separated in energy by five keV or more from photons emitted in the decay of ^{226}Ra or progeny.

(9) NCRP Report No. 58, 1978, p. 435 (1978).

National Bureau of Standards

Standard Reference Material 4950E

Correction of Standard

Reference time: April 1, 1984

Radium-226 originally present in standard

$$4.9314 \text{ g} \times 7.566 \times 10^{-11} \text{ g} = 3.731097 \times 10^{-10} \text{ g}$$

Time (t) in years since NBS standardization of solution

January 1, 1985 - April 1, 1984 = 0.75 years

Correction factor $= [1 - (4.3 \times 10^{-4})(t)]$

$= [1\ 9\ (4.3 \times 10^{-4})(0.75)]$

$= 0.9996775$

Radium-226 in standard solution as of January 1, 1985

$$3.731907 \times 10^{-10} \text{ g} \times 0.9996775 = 3.72989 \times 10^{-10} \text{ g}$$

Activity of radium-226 in standard solution

$$3.72989 \times 10^{-10} \text{ g} \times 0.990 \text{ Ci/g} = 3.692595 \times 10^{-10} \text{ Ci} = 369.260 \text{ pCi}$$

Acid Barium Chloride Solution

This solution was used to dilute the NBS radium-226 standard solution.

From page 592, Standard Methods for the Examination of Water and Wastewater. 15th Edition, 1980. APHA-AWWA-WPCF.

a. Stock barium chloride solution

Dissolve 17.79 g, $BaCl_2 \cdot 2H_0$) in distilled water and dilute to 1 L; 1 mL = 10 mg Ba.

b. Dilute barium chloride solution

Dilute 200.0 mL stock barium chloride solution to 1,000 mL as needed; 1 mL = 2.00 mg Ba^{+2}. Let stand 24 hours and filter through a membrane filter (0.45 µm).

c. Acid barium chloride solution

To 20 mL concentration HCl in a 1 L volumetric flask, add dilute $BaCl_2$ solution to the mark and mix.

APPENDIX 2.2

SLUDGE HANDLING AND DISSOLUTION PROCEDURES

The percent solids content calculated for each subsample obtained as described in Section 6.2 is given in Table A 2.2-1. Sample CL 6-4 was lost during the dissolution process.

Table A 2.2-1
Percent Solids Content of Sludge Samples

Sample	Mass of Wet Sludge (g)	Mass of Dry Sludge (g)	% Solid	Average % Solid for Sludge Bottle
RA 12-3	0.66227	0.29514	44.56	
RA 12-4	0.77292	0.38214	49.44	
RA 12-5	0.80002	0.34527	43.16	45.72
RA 114-4	0.50029	0.22229	44.43	
RA 114-6	0.57579	0.22774	39.55	
RA 114-7	0.69737	0.29773	42.69	42.23
CL 6-5	0.61381	0.22438	36.56	
CL 6-6	0.57978	0.22445	38.71	37.64
CL 18-1	0.36100	0.10983	30.42	
CL 18-2	0.57083	0.09353	16.38	
CL 18-3	0.42915	0.11582	26.99	24.60
A1-1	0.41125	0.08955	21.78	
A1-2	0.52847	0.15422	29.18	
A1-6	0.85797	0.22899	26.69	25.88
A2-1	0.66019	0.10027	15.19	
A2-2	0.77401	0.12233	15.80	
A2-3	0.70349	0.11402	16.21	15.73

For the dissolution procedure all samples were treated in the same manner. Each sample was quantitatively transferred from the vial into a 400 mL beaker, using a total of 25.0 mL of 0.05 M EDTA to aid in the transfer. Distilled water (250 mL) was added and the pH was adjusted to 10.5 with NaOH. The samples were then digested on a hot plate at 90°C for 12 hours.

Following the digestion, two different forms of solid material remained in the beaker. At the high pH of the solutions any iron present in the samples is precipitated as hydrous iron oxide. The characteristic red precipitate of this oxide was especially apparent in the Rio Algom sludge. In addition to the red iron precipitate, solid particles visually similar to sand grains were observed. To correct for the undissolved material, each solution was filtered through a borosilicate glass fiber filter mat in a pre-weighed Gooch crucible. The filtered supernatant solution, including the washings, was then quantitatively transferred to a 500-mL volumetric flask and diluted to the mark. The precipitate in the Gooch crucible was washed with 5 mL of concentrated hydrochloric acid to dissolve the hydrated iron oxide and any other acid soluble material and the residue was again washed with distilled water. Both the washings and the hydrochloric acid solution were transferred quantitatively to a 100-mL volumetric flask and diluted to the mark. The remaining undissolved solid was dried to constant weight in the crucible at 100°C.

Table A 2.2-2 shows the relationship between the dry weight of the sludge and the undissolved residue. The undissolved material ranged between 7.6 and 9.8% for the Rio Algom sludge and between 2.0 and 4.1 for the Cluff Lake sludge. It is interesting to note that the residue in the lime-treated samples (A1-1 to A2-3) was approximately 2% while in the untreated samples from Cluff Lake the quantity of undissolved sludge was almost double that amount, or about 4%.

Table A 2.2-2
Percent Undissolved Sludge After Dissolution Procedure

Sludge	Mass of Dry Sludge (g)	Mass of Undissolved Sludge (g)	% Undissolved Sludge	Average % Undissolved Sludge
RA 12-3	0.29514	0.0261	8.8	
RA 12-4	0.38214	0.0355	9.3	
RA 12-5	0.34527	0.0262	7.6	8.6
RA 114-4	0.22229	0.0186	8.4	
RA 114-6	0.22774	0.0224	9.8	
RA 114-7	0.29773	0.0266	8.9	9.0
CL 6-5	0.22438	0.0076	3.4	
CL 6-6	0.22445	0.0083	3.7	3.5
CL 18-1	0.10983	0.0043	3.9	
CL 18-2	0.09353	0.0038	4.1	
CL 18-3	0.11582	0.0047	4.1	4.0
A1-1	0.08955	0.0024	2.7	
A1-2	0.15422	0.0030	2.0	
A1-6	0.22899	0.0045	2.0	2.2
A2-1	0.10027	0.0020	2.0	
A2-2	0.12233	0.0024	2.0	
A2-3	0.11402	0.0022	2.0	2.0

Samples of the supernatant from the RA 12, RA 114, CL 6 and CL 18 bottles were obtained by allowing the wet sludge to settle and then withdrawing approximately 100 mL of the supernatant from each bottle. To remove suspended particulates, the supernatant was filtered through a 0.45 µm filter.

APPENDIX 2.3

Elemental Analysis of Sludge by Inductively Coupled Plasma (ICP) Spectroscopy

1. Introduction and General Discussion of the Measurement Method

The objective of these analyses was to determine the elemental composition of sludge samples from the Rio Algom and Cluff Lake mines. Emphasis was placed on measurement of the metal content of the samples. For this reason inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was chosen as the analytical method for the study. The high temperature of the ICP, in the range of 6,000 K (41,42,43) ensures complete dissociation of almost all molecules introduced into the plasma and prevents the formation of metal oxides in the analytical viewing zone. This eliminates two of the most common interferences in flame spectroscopy (44,45). The ICP has good sensitivity for most metallic and non-metallic elements, has a wide linear dynamic range and has excellent simultaneous multielement capabilities. The ICP yields information about atomic species only; it does not give information about the oxidation state or molecular structure of an element in the original material.

In any analytical procedure possible matrix effects must be considered. Although use of the ICP minimizes most matrix effects, it does not completely eliminate them. One problem with ICP and flame techniques is the effect of the presence of easily ionizable elements (EIE) in the material. In the dissolution procedure used in this work, the sodium salt of ethylenediamine tetracetic acid was employed (EDTA). Sodium, an easily ionizable element, is consequently present at relatively high concentrations in the dissolved sludge. Since the sludge is composed mainly of barium sulphate the presence of barium, another EIE, may also contribute to matrix effects.

In flame emission the presence of EIE's leads to enhancement of emission intensities for other elements present in the sample. With the ICP, the problem is more complex. The magnitude and direction of the matrix effect due to EIE's depends on the observation height or viewing zone utilized in the plasma. The viewing zone in the ICP is generally quoted in units of mm above the load coil (l.c.) which provides the radio-frequency power necessary to sustain the plasma. At lower observation heights (46,47) within approximately 15 mm above l.c., both neutral atom and ion line emission intensities are enhanced. At very low heights, the enhancement is greater for ion lines than for neutral atom lines. In the vicinity of 15 mm above l.c., the matrix effect changes from enhancement to depression of the analyte emission intensity. The point at which this crossover occurs depends upon the ionization potential of the element and upon whether the line is a neutral atom or ion line.

In this study, the viewing zone was centered at 17 mm above the l.c. This means that for most neutral atom lines, there should be little enhancement or depression of emission intensities due to the presence of EIE's. For most ion lines the result is a depression of the emission intensities.

To compensate for the presence of EIE's and other possible matrix effects in the sludge samples, the technique of standard addition was chosen. In the standard addition technique a known quantity of the analyte element is added to the unknown solution. For this technique to be applicable the response of the instrument to the analyte concentration must be linear (48). To check for linearity, a three point standard-addition procedure often is performed. In the work reported here, two different but accurately known quantities of each analyte of interest were added to separate aliquots of the sample solution. The sample solution without added analyte and the two standard-addition solutions were then measured. The total concentration of the analyte in the standard-addition solutions was chosen to be of approximately double the unknown concentration. Usually this means that a preliminary analysis is necessary to obtain approximate values. Once the standard addition analyses have been performed the emission intensity is graphed as a function of the added analyte concentration. The unknown concentration is then obtained from the x-intercept of the plot. Since the unknown and the standard addition solutions are measured under identical conditions and in the same matrix, matrix interferences are vitually eliminated.

In this study, only major elements were determined using the standard addition technique. These elements were barium, sulfur, calcium, iron, aluminum, magnesium, manganese, and zinc.

2. Preparation of Solutions for the Standard Additions Procedure

As mentioned previously, a preliminary analysis was required to determine the conditions for the standard addition. The preliminary analysis was performed by Sherritt-Gordon Mines Ltd., Fort Saskatchewan, Alberta. Nine elements were determined. Barium was analyzed using atomic absorption, and Ca, Al, Si, Fe, Zn, Mn and Pb by ICP. Sulfur could not be deterined because the Sherritt-Gordon ICP does not have a sulfur channel. The results are shown in Table 2.3-1, 2.3-2, and 2.3-3. On the basis of these results standard-addition concentrations were calculated and prepared for eight elements: Ba, S, Ca, Al, Fe, Mg, Mn and Zn.

Table 2.3-1. Preliminary Analysis of Rio Algom Sludge

Sample #	Ba %	Ca %	Al %	Si %	Fe %	Zn ppm	Mg ppm	Mn ppm	Pb ppm
RA 12-3	37.9	3.13	2.10	0.388	3.21	211	152	261	286
RA 12-4	37.0	2.86	2.00	0.456	3.05	235	126	248	266
RA 12-5	42.3	3.13	2.17	0.298	3.13	301	144	266	497
RA 114-4	40.4	3.10	2.06	0.790	3.18	209	190	258	82
RA 114-6	44.3	3.45	2.37	0.667	3.64	498	175	290	<D.L.
RA 114-7	39.5	2.99	2.11	0.656	3.16	264	135	254	251
Supernatant (all values ppm)									
RA 114	<1	424	<0.1	2.42	<0.005	<0.005	3.8	0.5	0.5

D.L. - Detection Limit

Table 2.3-2. Preliminary Analysis of Cluff Lake Sludge

Sample #	Ba %	Ca %	Al %	Si %	Fe %	Zn ppm	Mg ppm	Mn ppm	Pb ppm
CL 6-5	33.1	0.927	5.16	0.378	0.508	104	762	419	334
CL 6-6	34.6	0.943	5.12	0.331	0.506	388	748	415	216
CL 18-1	37.8	0.921	5.04	0.821	0.498	156	847	393	131
CL 18-2	35.5	1.10	5.05	0.692	0.501	523	1166	434	120
CL 18-3	34.1	0.952	5.12	0.487	0.510	342	811	396	<D.L.
Supernatant (all values ppm)									
CL 1	<D.L.	162	0.40	0.11	0.07	<D.L.	65	4.93	0.36
Supernatant (all values ppm)									
CL 6	<D.L.	153	0.50	0.14	0.24	<D.L.	67	5.85	0.37

D.L. - Detection Limit

Table 2.3-3. Preliminary Analysis of Cluff Lake Sludge (STS A-1, A-2)

Sample #	Ba %	Ca %	Al %	Si %	Fe %	Zn ppm	Mg ppm	Mn ppm	Pb ppm
A-11	27.2	3.15	5.09	0.914	0.017	<D.L.	12200	993	10700
A-12	28.4	2.82	5.20	0.958	0.016	460	5180	614	9300
A-13	35.2	2.71	4.73	0.795	0.014	<D.L.	7020	585	8450
A-21	42.3	2.60	6.02	0.811	0.016	<D.L.	12500	1420	8900
A-22	35.1	2.09	4.62	0.542	0.011	<D.L.	6370	574	7620
A-26	36.0	1.92	4.61	0.523	0.010	<D.L.	4560	1020	7670

D.L. - Detection Limits

Because each element was present at differing concentration levels, it was necessary to prepare more than one set of standard-addition solutions for each sample. For example, to analyze for barium it was necessary to dilute the dissolved sludge solutions by a factor of ten. At this concentration level the minor elements magnesium, manganese and zinc are present at concentrations less than the detection limit of the analysis and so a second set of standard-addition solutions had to be prepared on undiluted solutions for measurements of these elements.

For an individual sample at each concentration level, that is, for one set of standard-addition solutions, three solutions were prepared. The first solution was simply the unknown solution diluted with distilled water to an appropriate concentration level for the analysis. The second and third solutions contained an identical quantity of the unknown solution and in addition, for each element a volume of stock standard solution sufficient to approximately double the concentration of the element. For example, if the preliminary analysis showed that the zinc concentration in the sludge solution was approximately 2 mg/L sufficient stock zinc solution was added to the second and third solutions to give an increase in the total zinc level of 2 and 4 ppm respectively. All additions of the stock standards were made using a 1000-µL variable Eppendorf pipette.

The Eppendorf pipette was calibrated with one pipette tip to give an estimate of its accuracy and precision. The pipette was calibrated at settings of 250 µL, 500 µL, and 1000 µL. At each setting the pipette was filled with distilled water and emptied a total of ten times into a weighing bottle. From the weight and density of the distilled water, the volume delivered by the pipette at each setting was calculated. The trial was repeated five times for each volume. The uncertainty in the volume dispensed by the pipette was found to be of the order of ± 1 µL for each setting.

Because of the large number of pipettings required, individual pipette tips were not calibrated. However, the same pipette tip was used for a given element in all solution preparations. The variability between pipette tips has been previously studied (49) and has been found to be of the order of one percent or less for high quality tips provided by the manufacturer (this assumes that the measurements were all made in a consistent way by the same operator, as was the case here).

3 Instrumentation and Measurement Procedures

A commercially available 27.12 MHz radiofrequency inductively coupled plasma source coupled to a direct reader spectrometer was used (Applied Research Laboratories, Irvine, Calif., Model 16000). Plasma operating conditions and flow rates were as listed in Table 2.3-4. All samples were introduced as aerosols using a standard concentric gas nebulizer.

Table 2.3-4. Inductively Coupled Plasma Operating Conditions

Forward Power	1.25 kW
Reflected Power	< 0.05 kW
Frequency	27.12 MHz
Coolant gas flow rate	10 L/min
Auxiliary gas flow rate	0.65 L/min
Nebulizer gas flow rate	0.5 L/min
Viewing zone	17 mm above load coil

The ARL direct reader spectrometer coupled to the plasma source has provision for the simultaneous measurement of thirty-four different wavelengths. Because cadmium is measured at two wavelengths, this corresponds to a measurement capability for thirty-three elements. Table 2.3-5 lists the elements that can be determined and the wavelengths of the emission lines used for each, along with typical detection limits. Channels not operational at the time of use were those for nitrogen, carbon and silicon; since EDTA contains both nitrogen and carbon, measurement of the concentrations of these elements in the sludge was not feasible. The absence of the silicon channel on the University of Alberta instrument meant that it was not possible to determine silicon using the standard-addition technique. However, the preliminary analysis at Sherritt-Gordon did measure silicon; these results therefore have been included with those of the standard-addition measurements, with recognition that their uncertainties are greater.

Standard solutions of all the elements listed in Table 2.3-5 were aspirated into the ICP at the beginning of data acquision. These solutions were used to determine the concentration of (1) all elements in the supernatant samples, (2) all elements in the hydrochloric acid solutions used to dissolve hydrous iron oxide plus other acid soluble components, and (3) all elements in the sludge samples not determined using the standard-additions technique.

Integration times were 10 seconds, and three replicate measurements were performed on each sample and standard solution.

Standard solutions of all the elements listed in Table 2.3-5 were aspirated into the ICP at the beginning of data acquision. These solutions were used to determine the concentration of (1) all elements in the supernatant samples, (2) all elements in the hydrochloric acid solutions used to dissolve hydrous iron oxide plus other acid soluble components, and (3) all elements in the sludge samples not determined using the standard-additions technique.

Table 2.3-5

List of Elements Available for Measurement on the ARL Direct Reader ICP-AES Instrument and the Detection Limits

Channel No.	Element	Wavelength (nm)	Detection Limit in µg/mL (parts per million)
1Zr	343.82	0.00354	
2Sr	407.78	0.00029	
3Ba	455.40	0.00077	
4Ni	231.60	0.0071	
5Al	237.34	0.07983	
6 B	249.68	0.00371	
7Mn	257.61	0.00179	
8Fe	259.94	0.00256	
9 N	174.37	not used	
10	P	178.29	0.0581
11	S	180.73	0.02662
12	Hg	184.95	0.03271
13	Mg	279.08	0.01663
14	As	189.04	0.02153
15	Sn	189.99	0.00995
16	Si	288.16	not used
17	C	193.09	not used
18	V	292.40	0.00348
19	Na	589.59	0.0405
20	Mo	202.03	0.00756
21	Cr	205.55	0.00437
22	Sb	206.83	0.02727
23	Ge	209.53	0.05726
24	Ca	317.93	0.00731
25	Zn	213.86	0.004
26	Cu	324.75	0.00854
27	Ag	328.07	0.00397
28	Pb	220.35	0.00535
29	Li	670.78	0.00142
30	Ti	337.28	0.00097
31	Cd1	226.50	0.00298
32	Cd2	228.80	0.00424
33	In	230.61	0.05473
34	K	766.49	0.09404

Integration times were 10 seconds, and three replicate measurments were performed on each sample and standard solution.

4. Results

4.1 Supernatant Solutions

Supernatant samples from the RA 12, RA 114, CL 6 and CL 18 bottles were aspirated into the ICP without dilution. The results of the measurements are summarized in Table 2.3-6. Elements not present at concentrations above the detection limit were: Zr, Ni, Sn, Cr, Sb, Ge, Cu, Pb, Ti, Cd and In. As expected, the barium concentrations are low, approximately 0.03 mg/L for the Rio Algom and 0.5 mg/L for the Cluff Lake supernatant solutions. Sulfur, likely present as excess sulfate, follows the reverse trend in concentration. In the Rio Algom supernatant solutions the sulfur concentration is in the range of 425 mg/L, while in those from Cluff Lake it is lower, approximately 250 mg/L. Major differences between the two localities include the high concentrations of manganese, magnesium and sodium in the Cluff Lake supernatant relative to Rio Algom. Also, trace levels of aluminum, arsenic and vanadium were found in the Cluff Lake solutions, but none of the three were detected in those from Rio Algom.

The uncertainty reported for each value in Table 2.3-6 is the uncertainty of the measurement step and is the relative standard deviation of the three individual measurements.

Sludge Samples

To simplify discussion of the results the results of the analyses have been divided into two sections. Table 2.3-7 shows the concentrations of the major elements, that is, those present in all sludges at the percent level. The minor or trace elements, listed in Table 2.3-8, include those elements present at concentrations below the percent level, and are given in μg per g

Table 2.3-6
Analysis of Supernatant from Cluff Lake and Rio Algom Sludge

Element	Sample Identification Rio Algom Bottle 2 (mg/L)	Rio Algom Bottle 14 (mg/L)	Cluff Lake Bottle 6 (mg/L)	Cluff Lake Bottle 1 (mg/L)
Sr	0.252 ±0.002	0.252 ±0.003	0.0688 ±0.0005	0.0756 ±0.0009
Ba	0.0293 ±0.0001	0.0233 ±0.0002	0.392 ±0.004	0.690 ±0.007
Al	B.D.L.	B.D.L.	0.0323 ±0.0003	0.0861 ±0.0007
B	0.0746 ±0.0005	0.0576 ±0.0006	0.266 ±0.004	0.287 ±0.003
Mn	0.733 ±0.007	0.578 ±0.006	6.09 ±0.06	7.32 ±0.07
Fe	0.0289 ±0.0002	0.0430 ±0.0003	0.103 ±0.001	0.342 ±0.003
S	423±3	428±2	324±2	184±2
Mg	3.82 ±0.02	4.01 ±0.04	93.6 ±0.1	99.3 ±0.1
As	B.D.L.	B.D.L.	0.0902 ±0.0004	0.1640 ±0.0003
V	B.D.L.	B.D.L.	0.0103 ±0.0001	B.D.L.
Na	1.27 ±0.02	1.20 ±0.03	177 ±2	191 ±3
Mo	B.D.L.	B.D.L.	0.0281 ±0.0001	0.0265 ±0.0002
Ca	539±2	540±2	210±1	204±2
Zn	0.0120 ±0.0002	0.00649 ±0.00014	B.D.L.	0.00565 ±0.00013
Li	0.309 ±0.004	0.292 ±0.009	B.D.L.	B.D.L
K	94.7 ±0.2	95.2 ±0.3	15.2 ±0.1	14.4 ±0.1
Si	-	2.42 ±0.04	0.140 ±0.006	0.110 ±0.002

[a] B.D.L. denotes Below Detection Limit. See Table 2.3-5 for detection limits.

Table 2.3-7. Major Elements Present in Sludge Samples

Sample #	Ba (%)	S (%)	Al (%)	Ca (%)	Fe (%)	Sr (%)	K (%)	Si (%)
RA 12-3	46.9 ± 2.0	15.6 ± 0.5	2.79 ± 0.07	4.06 ± 0.01	4.02 ± 0.09	0.410 ± 0.005	0.382 ± 0.004	0.388 ± 0.007
RA 12-4	36.7 ± 1.7	12.8 ± 0.4	2.53 ± 0.12	3.78 ± 0.08	3.90 ± 0.13	0.346 ± 0.001	0.319 ± 0.008	0.456 ± 0.009
RA 12-5	43.9 ± 0.6	14.8 ± 0.3	2.70 ± 0.03	4.24 ± 0.10	3.78 ± 0.16	0.384 ± 0.002	0.273 ± 0.005	0.298 ± 0.005
RA 114-4	43.4 ± 1.1	16.3 ± 0.1	2.71 ± 0.07	4.12 ± 0.13	4.49 ± 0.28	0.358 ± 0.004	0.434 ± 0.006	0.790 ± 0.008
RA 114-6	43.0 ± 1.2	14.4 ± 0.5	2.58 ± 0.09	3.98 ± 0.20	4.07 ± 0.18	0.416 ± 0.006	0.305 ± 0.004	0.667 ± 0.009
RA 114-7	47.2 ± 1.1	16.6 ± 0.3	2.63 ± 0.06	3.86 ± 0.11	4.05 ± 0.10	0.360 ± 0.001	0.249 ± 0.003	0.656 ± 0.008
CL 6-5	40.2 ± 1.0	14.9 ± 0.6	6.86 ± 0.19	1.30 ± 0.05	0.74 ± 0.02	0.296 ± 0.001	0.345 ± 0.004	0.378 ± 0.004
CL 6-6	39.8 ± 1.2	14.7 ± 0.5	6.86 ± 0.18	1.35 ± 0.02	0.75 ± 0.03	0.297 ± 0.003	0.430 ± 0.005	0.331 ± 0.003
CL 18-1	39.0 ± 2.1	21.5 ± 0.6	7.68 ± 0.19	1.30 ± 0.02	0.76 ± 0.05	0.282 ± 0.001	0.352 ± 0.003	0.821 ± 0.009
CL 18-2	39.3 ± 1.9	23.7 ± 0.7	9.01 ± 0.20	1.52 ± 0.06	0.79 ± 0.03	0.286 ± 0.004	0.830 ± 0.007	0.692 ± 0.011
CL 18-3	39.0 ± 0.7	21.9 ± 0.7	7.42 ± 0.16	1.37 ± 0.04	0.78 ± 0.02	0.297 ± 0.003	0.670 ± 0.006	0.487 ± 0.005
A2-1	30.6 ± 0.9	21.5 ± 0.5	6.88 ± 0.12	4.55 ± 0.20	1.59 ± 0.06	0.166 ± 0.001	0.120 ± 0.002	0.914 ± 0.007
A2-2	34.4 ± 0.6	15.4 ± 0.1	6.80 ± 0.07	4.22 ± 0.21	1.43 ± 0.05	0.148 ± 0.001	0.199 ± 0.003	0.958 ± 0.012
A2-3	33.6 ± 0.6	18.5 ± 0.6	6.44 ± 0.15	3.86 ± 0.14	1.28 ± 0.08	0.158 ± 0.002	0.205 ± 0.002	0.795 ± 0.009
A1-1	38.2 ± 0.3	24.0 ± 0.3	8.58 ± 0.12	3.59 ± 0.02	1.37 ± 0.09	0.186 ± 0.002	0.434 ± 0.005	0.811 ± 0.008
A1-2	38.1 ± 1.4	18.9 ± 0.5	4.98 ± 0.09	3.13 ± 0.10	1.14 ± 0.08	0.171 ± 0.001	0.251 ± 0.003	0.542 ± 0.006
A1-6	40.1 ± 1.6	16.4 ± 0.1	6.69 ± 0.11	2.68 ± 0.13	1.14 ± 0.02	0.161 ± 0.001	0.167 ± 0.002	0.523 ± 0.009

Table 2.3-8. Trace Elements Present in Sludge Samples

Sample #	Mg (ppm)	Mn (ppm)	Zn (ppm)	B (ppm)	Cu (ppm)	Pb (ppm)	V (ppm)	Cr (ppm)
RA 12-3	340 ± 3	332 ± 5	458 ± 16	96 ± 3	145 ± 1	297 ± 1	17.6 ± 0.2	22.9 ± 0.1
RA 12-4	299 ± 5	321 ± 4	312 ± 12	226 ± 7	130 ± 1	259 ± 1	17.7 ± 0.1	25.0 ± 0.1
RA 12-5	369 ± 11	342 ± 9	422 ± 13	197 ± 6	116 ± 1	247 ± 1	14.3 ± 0.1	25.2 ± 0.1
RA 114-4	635 ± 18	331 ± 11	322 ± 16	572 ± 9	156 ± 2	348 ± 1	15.3 ± 0.1	30.3 ± 0.1
RA 114-6	484 ± 11	322 ± 6	311 ± 13	300 ± 4	206 ± 3	365 ± 2	24.3 ± 0.3	28.6 ± 0.1
RA 114-7	402 ± 16	335 ± 11	341 ± 10	418 ± 5	130 ± 1	309 ± 1	23.3 ± 0.2	25.4 ± 0.1
CL 6-5	1935 ± 21	594 ± 11	183 ± 4	126 ± 3	81 ± 1	566 ± 3	58.3 ± 0.4	32.3 ± 0.2
CL 6-6	1564 ± 28	592 ± 9	540 ± 15	74 ± 2	48 ± 1	514 ± 2	48.3 ± 0.2	29.8 ± 0.1
CL 18-1	2311 ± 74	576 ± 25	319 ± 11	454 ± 7	141 ± 2	805 ± 4	82.2 ± 0.2	61.2 ± 0.2
CL 18-2	2550 ± 160	637 ± 30	798 ± 27	443 ± 9	200 ± 3	786 ± 3	84.1 ± 0.5	45.7 ± 0.2
CL 18-3	2119 ± 55	575 ± 9	509 ± 17	80 ± 2	182 ± 2	713 ± 2	67.9 ± 0.3	36.9 ± 0.1
A2-1	1258 ± 31	241 ± 8	1460 ± 58	331 ± 8	111 ± 3	144 ± 1	B.D.L.	7.9 ± 0.1
A2-2	1397 ± 66	228 ± 9	788 ± 32	46 ± 1	91 ± 1	290 ± 1	13.6 ± 0.1	38.2 ± 0.1
A2-3	1127 ± 47	214 ± 3	1420 ± 60	12 ± 1	96 ± 1	169 ± 1	B.D.L.	15.0 ± 0.1
A1-1	1200 ± 100	242 ± 15	2030 ± 80	371 ± 6	174 ± 6	722 ± 3	63.6 ± 0.2	6.4 ± 0.1
A1-2	799 ± 70	169 ± 3	755 ± 34	122 ± 5	88 ± 1	449 ± 3	40.8 ± 0.2	6.2 ± 0.1
A1-6	780 ± 49	157 ± 4	464 ± 17	121 ± 4	71 ± 1	366 ± 2	34.5 ± 0.2	31.1 ± 0.3

B.D.L. - Below Detection Limit

Table 2.3-9. Average Concentrations for Measured Elements in Cluff Lake and Rio Algom Sludge Samples

	Major Elements, expressed as percent							Trace Elements, expressed as µg per g (ppm)							
Bottle #	Ba	S	Al	Ca	Fe	Sr	K	Mg	Mn	Zn	B	Cu	Pb	V	Cr
RA 2	42.5	14.4	2.67	4.03	3.90	0.380	0.325	336	332	397	173	130	268	16.5	24.4
RA 14	44.5	15.8	2.64	3.99	4.20	0.378	0.329	507	329	325	430	164	341	21.0	28.1
C L6	40.0	14.8	6.86	1.32	0.74	0.296	0.388	1750	593	362	100	64	540	53.0	31.0
C L18	39.1	22.4	8.04	1.40	0.78	0.285	0.617	2327	596	542	326	174	768	78.1	47.9
A2	32.9	18.5	6.71	4.21	1.43	0.157	0.175	1261	228	1223	128	99	301	13.6	20.4
A1	38.8	19.8	6.75	3.13	1.22	0.173	0.284	926	189	1083	205	111	512	46.3	14.6

(parts per million or ppm). All values have been calculated on the basis of weight of dried sludge sample. The average concentrations have been summarized in Table 2.3-9.

It must be emphasized that most of the major elements were measured using the standard-addition method while the trace elements, with the exception of magnesium, manganese and zinc, were measured using standardization with aqueous standards of each element. Consequently, the uncertainties in the results for each group have been determined differently.

For the standard-addition method (50) the standard deviation for the x-intercept, the concentration of the element in the sludge sample, was calculated. This uncertainty has been quoted in Tables 2.3-7 and 2.3-8 along with the respective concentrations for each element. For the other elements the concentrations were determined using the same sample solutions as for the standard-addition method. This means that for each trace element the concentrations quoted in Tables 2.3-7 and 2.3-8 are the average of three replicate measurements and the uncertainties are the standard deviations of the replicates. Again, the uncertainties are included in Tables 2.3-7 and 2.3-8.

Only those elements present at concentrations above the detection limits of Table 2.3-5 are listed in Tables 2.3-7 and 2.3-8. Those elements not present at detectable concentrations are: Zr, Ni, Hg, As, Sn, Mo, Sb, Ge, Ag, Li, Ti, Cd and In. For most of the trace elements reported in Table 2.3-8 the uncertainties between samples are low. The exceptions are vanadium and chromium; for these elements the concentration in the dissolved sludge samples was close to the detection limit for the element, leading to higher uncertainties in the results.

Comparison of these data with the preliminary results given in Tables

2.3-1 to 2.3-3 shows in most cases that matrix effects due to the high sodium and barium levels in the sludge samples caused depression of the emission intensities, as was discussed in Section 1 of this Appendix.

The variation in the analytical results between samples from individual bottles and between different bottles of sludge from the same mine give an estimate of the sampling and analytical uncertainty. Since only three samples were taken from each of two bottles for analysis, it is difficult to obtain a precise estimate of the sampling error. However, some trends can be noted. Table 2.3-9 lists the average value for each major element in each bottle of sludge. The average values for each bottle compare fairly well; that is, they agree within the measurement uncertainties quoted in Tables 2.3-7 and 2.3-8 for the Rio Algom sludge samples. Agreement within the Cluff Lake bottles was not as good. This could possibly be attributed to the smaller sample sizes used in the dissolution step. It must be noted that samples A1 and A2 were taken from different ponds at Cluff Lake. The composition therefore would not be expected to be similar.

There are several marked differences between the Cluff Lake and Rio Algom sludge samples. One interesting comparison is the sulfur content of the two sludges. The Cluff Lake sludge has a sulfur concentration over 20%, a value considerably higher than the approximately 15% found in Rio Algom sludge. This may relate to the visual indication of the presence of sulfide in the Cluff Lake sludge samples. Although some H_2S was likely lost in the drying process, a higher sulfide content and therefore a higher sulfur concentration might be expected as compared to the Rio Algom samples. Estimation of sulfide to sulfate ratios is not feasible in these measurements since the ICP is only capable of measuring elemental composition.

In the dissolution procedure, the red precipitate characteristic of hydrous iron oxide was observed in the Rio Algom samples but not in the Cluff Lake samples. The ICP analysis showed a much higher iron content of approximately 4% for the Rio Algom samples as compared to the approximately 0.75% found in the Cluff Lake samples.

Significant differences were noted in the calcium, magnesium and aluminum concentrations of the sludges from the two mines. For Cluff Lake the calcium, magnesium and aluminum concentrations were 1.4%, 0.21% and 7.5% respectively compared to 4%, 4% and 0.05% respectively for the Rio Algom sludge.

Most of the elements measured gave reasonable agreement between individual subsamples and between different bottles of sludge from the same site. For silicon, however, relative standard deviations within individual bottles were as high as 50%. Variation between bottles ranged up to 100%. This variation could possibly be explained by leaching of differing amounts of silicon from sand in the sludge. Small variations in the composition and amount of sand might cause relatively large variations in the measured values for silicon. A similar variability was observed with boron.

For the lime treated sludge samples, considerable variation was noted between individual subsamples for all elements. The addition of lime has apparently introduced a large variability in composition. The iron content of the Cluff Lake samples not treated with lime is quite low, about 0.75%. In comparison, the concentration in the lime treated samples is approximately double, on the order of 1.4%. Since lime is predominantly calcium carbonate the calcium content should be much higher in the lime treated samples and this was found to be the case. The calcium concentration in the lime treated samples was found to be approximately 4% compared to 1.5% for the untreated samples. Magnesium carbonate is usually present in lime. However, the magnesium concentration (0.1%) was lower in the lime treated samples than in the untreated samples (0.2%). The supernatant solution for the lime treated samples was not analyzed. It would be expected, however, that the magnesium concentration would be higher in the lime treated supernatants than in the untreated supernatants.

APPENDIX 2-4

Barium Determinations

Reagents

Nitric acid used was from Seastar Chemicals (Sidney, B.C.). A 10,000 ppm Ba standard solution (Spex Industries) was used to prepare a 1 µg/g Ba working standard solution. Distilled water was further purified by passage through a column of mixed strong acid and strong base ion exchange resins (Amberlite MB-3 Rohm and Haas Co.).

Procedure

A 0.5 mL portion of culture supernatant was combined with 0.1 mL concentrated HNO_3. Aliquots of 5 µL to 500 µL were diluted to 10 mL with deionized water prior to atomic absorption analysis. Standards for the calibration curve were prepared by diluting 0.25 to 1.5 mL of 1 µg/g Ba standard solution and 1 drop of concentrated HNO_3 to 10 mL with water. All samples were prepared so as to give an absorbance of approximately 0.1.

The atomic absorption measurements were made on a Perkin-Elmer Model 5000 spectrophotometer with an HGA 2200 furnace, an AS-1 autosampler and a PRS-10 Printer sequencer. Injected volumes were 20 µL. Pyrolytic graphite tubes with platforms (Perkin-Elmer part No. B012-1091) were used. Operating conditions were taken from Perkin-Elmer Analytical Methods for Atomic Absorption Spectroscopy using the HGA Graphite Furnace and were as follows: wavelength, 553.6 nm; slit width, 0.14 nm; integration time, 8 seconds; drying temperature and time, 110°C, 30 seconds; charring temperature and time, 600°C, 30 seconds; atomizing temperature and time, 2700°C, 8 seconds; purge gas, argon; hollow cathode lamp current, 25 ma. The gas flow was 40 mL/minute for the first 7 seconds of atomization and 300 mL/minute at other times. Working calibration curves were linear over the range 0 to 1.09×10^{-6} M barium. Blanks were run after every two sample measurements. Samples were injected at least twice.

Results of Barium Determinations for Microbiological Study of Effect of Lactate Concentrations

Sample #	Conc. of Lactic Acid (mg/L)	$\frac{\mu g\ Ba}{mL}$	Total mmol Ba^{2+}
Rio Algom			
10	0	1.4	0.002
11	500	1.6	0.002
12	1500	156	0.172
13	2500	178	0.196
14	3500	244	0.268
3	4000	74	0.081
Cluff Lake Set No. 1			
5	0	25.0	0.027
6	300	67.2	0.074
7	1500	109	0.120
8	3000	149	0.164
9	4000	91.9	0.101
1	6000	240	0.264
Cluff Lake Set No. 2			
1	0	0.69	0.0008
2	300	52.8	0.058
3	1500	93.6	0.103
4	2500	218.4	0.240
5	3000	193.2	0.212
6	3500	168.0	0.185
7	4000	143.1	0.157
8	6000	90.0	0.099

$$\text{Total mmol } Ba^{2+} = \frac{\left(\frac{\mu g\ Ba}{mL}\right)(151\ mL)}{(137\ mg/mmol)(1000\ \mu g/mg)}$$

Results of Barium Determinations for Microbiological Rate Experiment

Sample #	Day	$\frac{\mu g\ Ba}{mL}$	Total mmol Ba[a]
1	1	0.2	0.0002
2	3	0.6	0.0006
3	5	49.3	0.054
4	6	50.1	0.055
5	7	57.3	0.063
6	8	52.0	0.057
7	9	51.7	0.057
8	12	70.4	0.077
9	14	78.8	0.087
10	19	73.2	0.080
11	21	105.6	0.116
12	51	163.2	0.179

[a] Total calculated by the expression:

$$\text{Total mmol Ba}^{2+} = \frac{\left(\frac{\mu g\ Ba}{mL}\right)(151\ mL)}{\left(137.33\ \frac{mg}{mmol}\right)\left(1000\ \frac{\mu g}{mg}\right)}$$

APPENDIX 2.5
Calcium Determination

Reagents and Solutions

All chemicals were of reagent grade quality. Distilled water was further purified by passage through a column of mixed strong acid and strong base ion exchange resins (Amberlite MB-3, Rohm & Haas Co.).

Standard EDTA solution: A 0.005 M solution was prepared by dissolving 0.9305 g of $Na_2H_2EDTA \cdot 2H_2O$ (Fisher) in water and diluting to 500 mL. A 5-mL portion of this stock solution was diluted to 100 mL with water to give a 0.00025 M working solution.

Standard calcium solution was prepared by dissolving 1.248 g $CaCO_3$ (BDH) in 30 mL of 1 M HCl and diluting to 500 mL with water. This solution was diluted by a factor of 100 to give a working solution containing 10 µg Ca per mL.

Calcein indicator solution: Approximately 20 mg of Calcein (Fisher) was dissolved in 25 mL water and the minimum amount of 0.1 M KOH, then diluted to 1 litre. This solution deteriorates rapidly unless kept frozen and protected from light.

Potassium hydroxide - potassium cyanide solution: approximately 1 g of KCN (Fisher) and 5.6 g KOH (Baker) were dissolved in 100 mL of water to give a solution 0.15 M in KCN and 1 M in KOH.

Procedure

For the titration a 5-mL syringe was filled with 0.00025 M EDTA solution and weighed to the nearest milligram. In a small beaker were placed the following: 1 mL KCN-KOH solution, 1 mL water, 4 drops Calcein indicator solution and 1 mL calcium standard or 1 mL water for blank or 0.50 to 0.75 mL sample (diluted 1:10). A small stirring bar was added and the solution titrated with 0.00025 M EDTA under ultraviolet radiation until the green fluorescence disappears. The syringe was weighed after the titration and the weight of EDTA solution required determined by difference. The ultraviolet radiation was provided by a Chromatovue light enclosure (Ultraviolet Light Products Inc.).

Method from (51).

Calculations for Set No. 1

From the weight of EDTA taken the volume of EDTA was determined by dividing by the density of water at the temperature of water at the time of titration. The µg Ca in 0.75 ml of the 1:10 diluted sample solution was then determined as follows:

$$\mu\text{g Ca} = \text{mL EDTA (M EDTA)}\left(40.08\ \frac{\text{mg Ca}}{\text{mmol}}\right)(1000\ \mu\text{g/mg})$$

The millimoles of Ca present in the original sample bottles was calculated as follows:

$$\text{mmol Ca} = (\mu\text{g Ca})\left(\frac{\text{mL samp. in bottle}}{\text{0.075 mL used for titn.}}\right)\left(\frac{\text{mL tot. orig. sample}}{\text{mL sample taken}}\right)\left(\frac{10^{-3}\text{ mg}/\mu\text{g}}{\text{40.08 mg Ca/mmol}}\right)$$

Table 1. Data showing volumes of supernatant taken and final volumes after acidification and dilution for Set No. 1.

Sample #	Total Original Sample Volume (mL)	Sample Taken From Total (mL)	Sample After Acidification and Dilution (mL)
5	151	79	132
6	151	71	130
7	151	75	130
8	151	73	130
9	151	74	130
1	151	69	130

Table 2. Results of analyses of Set No. 1 for calcium.

Sample #	WT EDTA	mL EDTA	µg Ca	mL Sample	$\frac{\text{Total Orig. Sample}}{\text{mL Orig. Sample Taken}}$	mmol Ca
5	0.524	0.525	5.26	132	$\frac{151.0}{79.0}$	0.441
5	0.551	0.552	5.53	132	$\frac{151.0}{79.0}$	0.464
5	0.520	0.521	5.22	132	$\frac{151.0}{79.0}$	0.438
6	0.877	0.879	8.81	130	$\frac{151.0}{7.10}$	0.810
6	0.888	0.890	8.92	130	$\frac{151.0}{71.0}$	0.820
6	0.865	0.867	8.69	130	$\frac{151.0}{71.0}$	0.799
6	0.863	0.865	8.67	130	$\frac{151.0}{71.0}$	0.797
7	0.907	0.909	9.11	130	$\frac{151.0}{75.0}$	0.793
7	0.895	0.897	8.99	130	$\frac{151.0}{75.0}$	0.783
7	0.901	0.903	9.05	130	$\frac{151.0}{75.0}$	0.788
8	1.113	1.116	11.18	130	$\frac{151.0}{73.0}$	1.00
8	1.085	1.088	10.90	130	$\frac{151.0}{73.0}$	0.975
8	1.099	1.102	11.04	130	$\frac{151.0}{73.0}$	0.988
9	0.974	0.977	9.79	130	$\frac{151.0}{74.0}$	0.864
9	1.003	1.006	10.08	130	$\frac{151.0}{74.0}$	0.890
9	0.984	0.987	9.89	130	$\frac{151.0}{74.0}$	0.873
1	0.899	0.902	9.04	130	$\frac{151.0}{69.0}$	0.856
1	0.897	0.900	9.02	130	$\frac{151.0}{69.0}$	0.854
1	0.895	0.898	9.00	130	$\frac{151.0}{69.0}$	0.852

The volume of total original sample was 151 mL in all cases. The volume of sample taken from these bottles (69 to 79 mL) was then acidified and diluted to approximately 130 mL. It was this solution which was diluted 1:10 and 0.50 to 0.75 mL portions were taken for titration.

Calculations for Set No. 2

The volume of EDTA was determined by dividing the weight of EDTA measured by the density of water at the temperature of the water at the time of titration. The μg Ca in 0.50 mL of the diluted (1:10) sample solution was determined as follows:

$$\mu g\ Ca = mL\ EDTA\ (M\ EDTA)(40.08\ \frac{mg\ Ca}{mmol})(1000\ \mu g/mg)$$

The millimoles of Ca present in the original sample bottles was calculated as in Set No. 1, except that 0.050-mL portions were taken for titration in all cases. The volume of original sample was 151 mL in all cases. The volume of sample taken from these bottles was then acidified with 5 mL of concentrated nitric acid. This solution was diluted 1:10 and 0.5 mL portion were taken for titration.

Table 3. Data showing volumes of supernatant taken and final volumes after acidification and dilution for Set No. 2.

Sample #	Total Original Sample Volume (mL)	Sample Taken From Total (mL)	Sample After Acidification (mL)
1	151	52	57
2	151	51	56
3	151	65	70
4	151	63	68
5	151	55	60
6	151	60	65
7	151	62	67
8	151	62	67

Table 4 Results of analyses of Set No. 2 for calcium

Sample #	WT EDTA	mL EDTA	µg Ca	mL Sample	Total Orig. Sample / mL Orig. Sample Taken	mmol Ca	Mean mmol Ca
1	0.530	0.531	5.32	57	151/52	0.432	
1	0.526	0.527	5.28	57	151/52	0.436	0.432
1	0.517	0.518	5.19	57	151/52	0.429	
2	0.675	0.677	6.78	56	151/51	0.561	
2	0.653	0.655	6.56	56	151/52	0.543	0.550
2	0.658	0.660	6.61	56	151/51	0.547	
3	0.811	0.813	8.15	70	151/65	0.661	
3	0.807	0.809	8.11	70	151/65	0.658	0.661
3	0.814	0.816	8.18	70	151/65	0.664	
4	0.917	0.919	9.21	68	151/63	0.749	
4	0.879	0.881	8.83	68	151/63	0.718	0.741
4	0.928	0.930	9.32	68	151/63	0.758	
5	1.044	1.046	10.48	60	151/55	0.861	
5	1.047	1.050	10.52	60	151/55	0.865	0.863
5	1.045	1.048	10.50	60	151/55	0.863	
6	0.984	0.986	9.88	65	151/60	0.806	
6	1.029	1.031	10.33	65	151/60	0.843	0.814
6	0.947	0.949	9.51	65	151/60	0.776	
6	1.016	1.018	10.20	65	151/60	0.832	
7	0.991	0.993	9.95	67	151/62	0.810	
7	1.022	1.024	10.26	67	151/62	0.835	0.824
7	1.014	1.016	10.18	[illegible]	151		

1	0.517	0.518	5.19	57	$\frac{151}{52}$	0.429	
2	0.675	0.677	6.78	56	$\frac{151}{51}$	0.561	
2	0.653	0.655	6.56	56	$\frac{151}{52}$	0.543	0.550
2	0.658	0.660	6.61	56	$\frac{151}{51}$	0.547	
3	0.811	0.813	8.15	70	$\frac{151}{65}$	0.661	
3	0.807	0.809	8.11	70	$\frac{151}{65}$	0.658	0.661
3	0.814	0.816	8.18	70	$\frac{151}{65}$	0.664	
4	0.917	0.919	9.21	68	$\frac{151}{63}$	0.749	
4	0.879	0.881	8.83	68	$\frac{151}{63}$	0.718	0.741
4	0.928	0.930	9.32	68	$\frac{151}{63}$	0.758	
5	1.044	1.046	10.48	60	$\frac{151}{55}$	0.861	
5	1.047	1.050	10.52	60	$\frac{151}{55}$	0.865	0.863
5	1.045	1.048	10.50	60	$\frac{151}{55}$	0.863	
6	0.984	0.986	9.88	65	$\frac{151}{60}$	0.806	
6	1.029	1.031	10.33	65	$\frac{151}{60}$	0.843	0.814
6	0.947	0.949	9.51	65	$\frac{151}{60}$	0.776	
6	1.016	1.018	10.20	65	$\frac{151}{60}$	0.832	
7	0.991	0.993	9.95	67	$\frac{151}{62}$	0.810	
7	1.022	1.024	10.26	67	$\frac{151}{62}$	0.835	0.824
7	1.014	1.016	10.18	67	$\frac{151}{62}$	0.829	
7	1.003	1.005	10.07	67	$\frac{151}{62}$	0.820	
8	0.904	0.906	9.08	67	$\frac{151}{62}$	0.739	
8	0.928	0.930	9.32	67	$\frac{151}{62}$	0.759	0.755
8	0.937	0.939	9.41	67	$\frac{151}{62}$	0.766	

APPENDIX 2.6

Sulfide Determination

Reagents

Reagent grade chemicals were used throughout. Distilled water was further purified by passage through a column of mixed strong acid and strong base ion exchange resins (Amberlite MB-3, Rohm and Haas Co.). The silver nitrate and potassium chloride solutions were prepared from primary grade materials and the molarities cross checked by direct titration of the KCl solution wth the $AgNO_3$ solution as described above.

Procedure

Excess liquid was decanted from the sludge in culture bottles. The remaining sludge suspension was shaken well and immediately poured into a tared 300-mL Erlenmeyer flask. The flask and contents were then weighed to the nearest milligram. About 50 mL of demineralized water and a stirring bar were added and the flask was connected to the sparging apparatus as shown in Figure 1.

Fifty mL of 0.1 M $AgNO_3$ were pipetted into the first test tube and 20 mL into the second test tube. The test tubes were connected to the apparatus and nitrogen gas was bubbled through the constantly stirred sludge solution in the Erlenmeyer flask at a rate of about 40 mL/minute. Approximately 6 M HCl was added from a buret with a pipet bulb at the top to force the acid into the flask. The acid was added in about 1-mL increments at about 1.5 minute intervals for the first 10 mL and then in 3-mL increments every 3 to 5 minutes until the reaction mixture was a pale yellow. During the initial stages of reaction the gas flow was increased slowly because of Ag_2S precipitation in the glass frit in the first test tube. After the last addition of acid the mixture was allowed to stir for 15 minutes with continuous N_2 passage. When the reaction was complete the Ag_2S was removed from the $AgNO_3$ in the first test tube (and the second test tube when necessary) by vacuum filtration on Whatman No. 2 paper and the test tube and precipitate rinsed well with demineralized water. The gas dispersion tube was soaked in concentrated HNO_3 to dissolve as much of the Ag_2S that had precipitated in the frit as possible. The filtrate was collected and a known excess of 0.1 M KCl added. The mixture was swirled, allowed to stand 3 to 5 minutes and then vacuum filtered to remove AgCl precipitate. Dextrin (0.2g) and 0.1% dichlorofluorescein indicator (10 drops) were added to the filtrate and the solution was then titrated with 0.1 M $AgNO_3$ to the first appearance of pink. All runs were carried out twice; values for the duplicate measurements are shown in the figure.

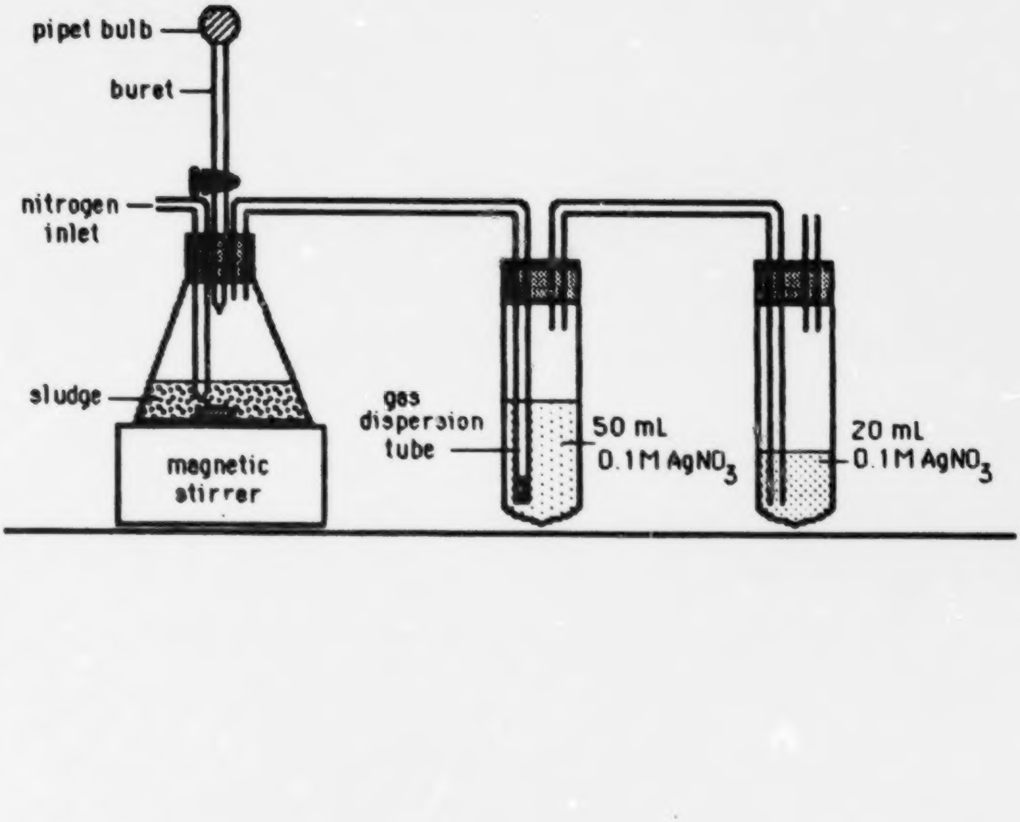
pipet bulb
buret
nitrogen inlet
sludge
magnetic stirrer
gas dispersion tube
50 mL
0.1M AgNO3
20 mL
0.1M AgNO3

Figure 1. Sulfide Apparatus

Table 1. Results for determination of sulfide in microbiology lactic acid experiments - Rio Algom

Sample No.	Conc. of Lactic Acid (mg/L)	Slurry Weight (g)	Average Total mmol S^{2-}	Total mmol Ba^{2+}
10	0	79.678	0.080	0.002
11	500	83.259	0.46	0.00
12	1500	76.530	1.110	0.172
13	2500	71.916	1.043	0.196
14	3500	70.504	1.128	0.268
3	4000	74.459	1.228	0.081

$$\text{Total mmol } S^{2-} = \left(\frac{\text{mmol}}{\text{g slurry}}\right)(\text{total wt slurry})$$

$$\text{Total mmol } Ba^{2+} = \frac{(\text{Total 151 mL volume})(\mu g\ Ba^{2+}/\text{mL})}{\left(137.33\ \frac{\text{mg}}{\text{mmol}}\ Ba^{2+}\right)\quad\left(1000\ \frac{\mu g}{\text{mg}}\right)}$$

Table 2. Results for determination of slufide in microbiology lactic acid experiments - Cluff Lake Set No. 1

Sample No.	Conc. of Lactic Acid (mg/L)	Slurry Weight (g)	Average Total mmol S^{2-}	Total MMol Ba^{2+}
5	0	44.494	0.534	0.027
6	300	80.484	1.851	0.074
7	1500	69.304	1.801	0.120
8	3000	67.282	3.162	0.164
9	4000	62.226	2.053	0.101
1	6000	55.936	1.007	0.264

$$\text{Total mmol } S^{2-} = \left(\frac{\text{mmol } S^{2-}}{\text{g slurry}}\right)(\text{total slurry weight})$$

$$\text{Total mmol } Ba^{2+} = \frac{(\text{Total volume})(\mu\text{g Ba/mL})}{\left(137.33\ \frac{\text{mg}}{\text{mmol}}\right)\left(1000\ \frac{\mu\text{g}}{\text{mg}}\right)}$$

Table 3. Results for determination of slufide in microbiology lactic acid experiments - Cluff Lake Set No. 2

Sample No.	Conc. of Lactic Acid (mg/L)	Slurry Weight (g)	Average Total mmol S^{2-}	Total mmol Ba^{2+}
1	0	0.708	0.0008	64.329
2	300	66.845	1.237	0.058
3	1500	63.622	1.386	0.103
4	2500	61.675	1.437	0.240
5	3000	65.783	1.875	0.212
6	3500	65.244	1.925	0.185
7	4000	63.254	1.727	0.157
8	6000	60.892	1.504	0.099

APPENDIX 3

Geochemical Modelling Programs, Operating Procedure and Sample Output

Appendix 3.1 Listing of SLUDGE Program

```
C PROGRAM TO TEST SATURATION WITH BARITE IN NATURAL
C WATERS OF VARYING IONIC STRENGTH, SULFUR CONC., BA CONC, AND PH.
      IMPLICIT REAL*8(A - Z)
      DATA ADH /0.5/, BDH /0.33/, CONC/28000./
      DATA KHSO4 /0.0102329/, KBA /.104712855E-09/
C ******INPUT IONIC STR (IST), TOTAL SULF CONC (TSULF), BA CONC(TBA)
C AND PH (PH)
      TEN = 0.01 / (10**10.)
   10 WRITE (6,20)
   20 FORMAT (' ', 'INPUT SOLUTION PARAMETERS IN THE FOLLOWING ORDER', /
     1       , 'IONIC STR, TOTAL SULF, TOTAL BA, AND PH', /)
      READ (5,30) IST, TSULF, TBA, PH
      WRITE (6,30) IST, TSULF, TBA, PH
   30 FORMAT (5F14.10)
      EPH = 10**(-PH)
C****CALCULATE ACTIVITY COEFF OF AQ SPECIES BY THE DAVIES EQ***
C**  G1 FOR MONOVALENT SPECIES AND G2 FOR DIVALENT SPECIES***
      LOGG1 = ((-ADH*IST**.5)/(1 + IST**.5) - 0.3*IST)
      LOGG2 = ((-ADH*4*IST**.5)/(1 + IST**.5) - 0.3*IST)
         G1 = 10**LOGG1
         G2 = 10**LOGG2
      WRITE(6,31) G1, G2
   31 FORMAT(' ACTIVITY COEFFICIENTS:',/,' MONOVALENT SPECIES = ',
     $   F5.3,'    DIVALENT SPECIES = ',F5.3,/)
C***CALCULATE THE MOLALITY OF SO4 AND HSO4 FOR THE GIVEN TSULF***
      RATIO = KHSO4 * G1 / (EPH*G2)
      MHSO4 = TSULF / (1 + RATIO)
      MSO4 = TSULF - MHSO4
C****CALCULATE THE AMOUNT OF SO4 AND BA2+ IN EQ WITH BARITE*****
C *** BASO4 = BA2 + SO4*** EQSULF = K**.5 ***AND K=10**-9.98
      EQSO4 = (KBA/G2**2.) ** 0.5
      EQBA = EQSO4
C***CHECK FOR SATURATION WITH BARITE***
      KTEST = TBA * MSO4 * (G2**2)
      IF (KTEST .GT. 0.) GO TO 40
      WRITE (6,60) EQSO4
      GO TO 130
   40 CONTINUE
      STEST = KBA - KTEST
      IF (STEST) 70, 90, 50
   50 CONTINUE
C*** CALCULATE THE AMOUNT OF BASO4 REQD TO BRING SOLN TO SATURATION
C**** POSITIVE ROOT OF THE QUADRATIC EQUATION ********
      BB = TBA + MSO4
      CC = (TBA*MSO4) - (KBA/G2**2)
      DD = BB ** 2 - 4 * CC
      MSAT = (-BB + DSQRT(DD)) / 2.
      WRITE (6,60) MSAT
   60 FORMAT (' ', 'THE SOLUTION IS UNDERSATURATED BY', F10.7, 3X,
     1       'MOLES OF BARITE')
      GO TO 110
   70 WRITE (6,80)
   80 FORMAT (' ', 'THE SOLUTION IS OVERSATURATED WITH BARITE')
      GO TO 130
   90 WRITE (6,100)
  100 FORMAT (' ', 'THE SOLUTION IS SATURATED WITH BARITE')
      GO TO 130
  110 CONTINUE
C *** ASSUME RA IS 28,700 pCi/g of SLUDGE ***
      GBA = MSAT * 233.3
      GRA = GBA * CONC
      IF (GRA .LE. TEN) GO TO 130
      WRITE (6,120) GRA
  120 FORMAT (' ', 'IF ALL OF THE ABOVE BARITE IS DISSOLVED,', /,
     1        ' THE CONCENRATION OF RADIUM IN THE SOLUTION WILL BE', /,
     2        3X,D14.7, ' pCi/g')
  130 WRITE (6,140)
  140 FORMAT (' ', 'DO YOU WISH TO CONTINUE OR STOP? (0=STOP,1=CONTINUE'
     1        )
      READ (5,150) ANS
  150 FORMAT (F3.0)
      IF (ANS .GT. 0) GO TO 10
      CONTINUE
      STOP
      END
End of file
```

Appendix 3.2 Listing of PHREEQE Program

```
C
C          *********************************************
C
C                          PROGRAM PHREEQE
C
C          D.L. PARKHURST, D.C. THORSTENSON, L.N. PLUMMER
C
C                VERSION CURRENT - JANUARY 12, 1981
C
C          *********************************************
C
C
C
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      REAL*8 SUNAME(10)
      COMMON /NEUT/ SUNAME,DNEUT,NSUM(10),NSUMS,LSUM(10,50),LPOS,LNEG
      INTEGER*4 IFILE
      MAXT=30
      MAXS=250
      MAXT1=31
      MAXM=20
      MAXEQ=50
      DO 10 I=1,MAXS
      NSP(I)=0
   10 CONTINUE
      IFILE=10
      CALL RDATA(IFILE)
   20 CONTINUE
C           SINGLE SIMULATION LOOP
      CALL READ
      ISTEP=0
C           SOLVE INITIAL SOLUTIONS
      DO 40 ISOL=1,2
      IF (ISOLV(ISOL).EQ.0) GO TO 40
      CALL SOLN(ISOL)
      IESPEC=IOPT(2)
      IF (IOPT(2).GE.2) IESPEC=0
      CALL PICK1
      CALL PTOT
      CALL KTEMP
      CALL MODEL
      IF (IOPT(2).LT.2) GO TO 30
      IESPEC=LNEG
      IF (ELECT.LT.0D0) IESPEC=LPOS
      CALL PICK1
      CALL KTEMP
      CALL MODEL
      TOTAL(ISOL,IESPEC)=TOT(IESPEC)
   30 CONTINUE
      IF (IASPEC.GT.0) TOTAL(ISOL,IASPEC)=TOT(IASPEC)
      CALL THORIT(T)
      TH(ISOL)=T
      THOR=T
      DIFFZ(ISOL)=ELECT
      CALL PSPEC
      CALL PLOOK
   40 CONTINUE
      IF (IOPT(3).EQ.0) GO TO 20
C            TAKE REACTION STEPS
      IF (NSTEPS.LE.0) NSTEPS=1
      DO 50 ISTEP=1,NSTEPS
      CALL STEP
      CALL PTOT
      CALL PICK2
      CALL KTEMP
      CALL KMIN
      CALL MODEL
      CALL PPHASE
      CALL PLOOK
      CALL PTOT
      CALL PSPEC
   50 CONTINUE
      CALL SAVE
      GO TO 20
      END
      SUBROUTINE READ
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5      NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6      MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      REAL*8 SUBS,SUB,TNAM
      DIMENSION ISUB(12),SUBS(12),LT(30),DTOT(30)
      DATA SUBS /'TEMP    ','MINERALS','SOLUTION','REACTION',
     1           'STEPS   ','ELEMENTS','SPECIES ','END     ',
     2           'LOOK MIN','SUMS    ','NEUTRAL '/
      REAL*8 NAMELK
      REAL*4 LKLOOK,LKOLK
      COMMON /LOOK/ NAMELK(40),LKOLK(40),LKLOOK(40),DHLOOK(40),
     1      ALOOK(40,10),CLOOK(40,10),LLOOK(40,10),NLOOK(40),
     2      LOOKFL(40),NLOOKS
      REAL*8 SUNAME(10)
      COMMON /NEUT/ SUNAME,DNEUT,NSUM(10),NSUMS,LSUM(10,50),LPOS,LNEG
      INTEGER*4 IFILE
      DATA NLKS,NSMS /0,0/
      DATA DELETE /'DELETE'/
      COMMON /OFFSET/ SIMIN(20)
   10 CONTINUE
      IERR=0
      ISOLV(1)=0
      ISOLV(2)=0
      NRMINS=0
      NLOOKS=NLKS
      NSUMS=NSMS
      DO 20 I=1,8
      ISUB(I)=0
   20 CONTINUE
C            READ TITLE CARD
      READ (5,420,END=410) TITLE
C            READ OPTION CARD
      READ 430, (IOPT(I),I=1,10),NSTEPS,NCOMPS,VO
      IF (IOPT(1).EQ.1) CALL PDATA
      PRINT 440, TITLE
      PRINT 450, (IOPT(I),I=1,10),NSTEPS,NCOMPS,VO
      IREAD=0
      IFILE=5
      GO TO 30
C      *****
      ENTRY RDATA(IFILE)
C      *****
      PRINT 460
      IREAD=1
   30 CONTINUE
C            READ SUBROUTINE CARD AND BRANCH
   40 CONTINUE
      READ (IFILE,470) SUB,ISOLN
      DO 50 I=1,11
      IF (SUB.NE.SUBS(I)) GO TO 50
      GO TO (60,70,110,150,170,180,220,400,260,350,390), I
   50 CONTINUE
      PRINT 480, SUB
      GO TO 40
C
C         .  READ TEMP DATA
C
   60 CONTINUE
      PRINT 490
      IF (IOPT(4).EQ.0) GO TO 40
      NTEMP=IOPT(4)
      IF (NTEMP.EQ.3) NTEMP=NSTEPS                                      B  840
      READ 500, (TSTEP(I),I=1,NTEMP)                                    B  850
      PRINT 510, (TSTEP(I),I=1,NTEMP)                                   B  860
      ISUB(1)=1                                                         B  870
      GO TO 40                                                          B  880
C                                                                       B  890
C           READ MINERAL DATA                                           B  900
C                                                                       B  910
   70 CONTINUE                                                          B  920
      PRINT 520                                                         B  930
      I=0                                                               B  940
   80 CONTINUE                                                          B  950
      I=I+1                                                             B  960
C           READ NAME ETC. FOR MINERAL                                  B  970
      READ 530, MNAME(I),NMINO(I),THMIN(I),LKTOM(I),DHMIN(I),MFLAG(I),SIB  980
     1MIN(I)                                                            B  990
      PRINT 540, MNAME(I),NMINO(I),THMIN(I),LKTOM(I),DHMIN(I),MFLAG(I),SB 1000
     1IMIN(I)                                                           B 1010
      IF (NMINO(I).EQ.0) GO TO 100                                      B 1020
      NRMINS=I                                                          B 1030
C           READ COEFFICIENTS FOR MINERAL                               B 1040
      K=NMINO(I)                                                        B 1050
      READ 550, (LMINO(I,J),CMINO(I,J),J=1,K)                           B 1060
      PRINT 560, (LMINO(I,J),CMINO(I,J),J=1,K)                          B 1070
C           READ ANALYTIC EXPRESSION COEFFICIENTS                       B 1080
      IF (MFLAG(I).EQ.0) GO TO 90                                       B 1090
      READ 570, (AMIN(I,J),J=1,5)                                       B 1100
      PRINT 580, (AMIN(I,J),J=1,5)                                      B 1110
   90 CONTINUE                                                          B 1120
      GO TO 80                                                          B 1130
  100 CONTINUE                                                          B 1140
      CALL MINCON                                                       B 1150
      CALL CHKMIN(IERR)                                                 B 1160
      ISUB(2)=1                                                         B 1170
      GO TO 40                                                          B 1180
C                                                                       B 1190
C           READ A SOLUTION                                             B 1200
C                                                                       B 1210
  110 CONTINUE                                                          B 1220
      PRINT 590, ISOLN                                                  B 1230
C           READ SOLUTION TITLE                                         B 1240
      READ 600, (HEAD(ISOLN,J),J=1,20)                                  B 1250
      PRINT 610, (HEAD(ISOLN,J),J=1,20)                                 B 1260
C           READ NTOTS,PH,EH                                            B 1270
      READ 620, NTOTS,IALK(ISOLN),IUNITS(ISOLN),PH,PE,TEMP(ISOLN),SDENS(B 1280
     1ISOLN)                                                            B 1290
      IF (SDENS(ISOLN).EQ.0.0) SDENS(ISOLN)=1.0                         B 1300
      PRINT 630, NTOTS,IALK(ISOLN),IUNITS(ISOLN),PH,PE,TEMP(ISOLN),SDENSB 1310
     1(ISOLN)                                                           B 1320
C           READ TOTALS                                                 B 1330
      DO 120 I=1,MAXT                                                   B 1340
      TOTAL(ISOLN,I)=0D0                                                B 1350
  120 CONTINUE                                                          B 1360
      IF (NTOTS.EQ.0) GO TO 140                                         B 1370
      READ 640, (LT(J),DTOT(J),J=1,NTOTS)                               B 1380
      PRINT 650, (LT(J),DTOT(J),J=1,NTOTS)                              B 1390
C           ZERO TOTAL AND INSERT VALUES                                B 1400
      DO 130 I=1,NTOTS                                                  B 1410
      TOTAL(ISOLN,LT(I))=DTOT(I)                                        B 1420
  130 CONTINUE                                                          B 1430
```

```
      CALL UNITS(ISOLN)
  140 CONTINUE
      TOTAL(ISOLN,1)=1D1**(-PH)
      TOTAL(ISOLN,2)=1D1**(-PE)
      ISOLV(ISOLN)=1
      ISUB(3)=1
      GO TO 40
C
C           READ REACTION DATA
C
  150 CONTINUE
      IF (NCOMPS.EQ.0) GO TO 40
      PRINT 660
C           READ COEFFICIENTS OF REACTION
      READ 670, (LREAC(I),CREAC(I),THMEAN(I),I=1,NCOMPS)
      PRINT 680, (LREAC(I),CREAC(I),THMEAN(I),I=1,NCOMPS)
      THREAC=0D0
      DO 160 I=1,NCOMPS
      THREAC=THREAC+THMEAN(I)*CREAC(I)
  160 CONTINUE
      ISUB(4)=1
      GO TO 40
C
C           READ STEPS DATA
C
  170 CONTINUE
      IF (NSTEPS.EQ.0.OR.IOPT(3).EQ.5) GO TO 40
      PRINT 690
      K=NSTEPS
      IF (IOPT(3).EQ.4) K=1
      READ 700, (XSTEP(I),I=1,K)
      PRINT 710, (XSTEP(I),I=1,K)
      ISUB(5)=1
      GO TO 40
C
C           READ ELEMENT CARDS
C
  180 CONTINUE
      PRINT 720
C           READ ELEMENTS UNTIL BLANK CARD
  190 CONTINUE
      READ (IFILE,730) TNAM,NELT,TGFW
      IF (IREAD.EQ.0) PRINT 740, TNAM,NELT,TGFW
      IF (NELT.EQ.0) GO TO 210
      IF (NELT.GT.3.AND.NELT.LE.MAXT) GO TO 200
      PRINT 750, NELT,TNAM,SUBS(6)
      STOP
  200 CONTINUE
      TNAME(NELT)=TNAM
      GFW(NELT)=TGFW
      GO TO 190
  210 CONTINUE
      ISUB(6)=1
      GO TO 40
C
C           READ SPECIES CARDS
C
  220 CONTINUE
      PRINT 760
C           READ SPECIES CARDS UNTIL BLANK CARD
```

```
  230 CONTINUE
      READ (IFILE,770) I
      IF (IREAD.EQ.0) PRINT 780, I
C           READ SPECIES NAME ETC.
      IF (I.EQ.0) GO TO 250
      IF (I.GT.0.AND.I.LE.MAXS) GO TO 240
      READ (IFILE,790) TNAM
      PRINT 750, I,TNAM,SUBS(7)
      STOP
  240 CONTINUE
      READ (IFILE,790) SNAME(I),NSP(I),KFLAG(I),GFLAG(I),ZSP(I),THSP(I),
     1DHA(I),(ADHSP(I,J),J=1,2),ALKSP(I)
      IF (IREAD.EQ.0) PRINT 800, SNAME(I),NSP(I),KFLAG(I),GFLAG(I),ZSP(I
     1),THSP(I),DHA(I),(ADHSP(I,J),J=1,2),ALKSP(I)
      IF (NSP(I).EQ.0) GO TO 230
C           READ LOG K DATA FOR SPECIES
      READ (IFILE,810) LKTOSP(I),DHSP(I),(ASP(I,J),J=1,5)
      IF (IREAD.EQ.0) PRINT 820, LKTOSP(I),DHSP(I),(ASP(I,J),J=1,5)
C           READ COEFFICIENTS
      K=NSP(I)
      READ (IFILE,830) (LSP(I,J),CSP(I,J),J=1,K)
      IF (IREAD.EQ.0) PRINT 840, (LSP(I,J),CSP(I,J),J=1,K)
      GO TO 230
  250 CONTINUE
      ISUB(7)=1
      CALL CHKSPE(IERR)
      GO TO 40
C
C           READ MINERALS TO LOOK AT
C
  260 CONTINUE
      PRINT 850
      I=NLKS
  270 CONTINUE
      I=I+1
      IF (I.LT.41) GO TO 280
      PRINT 860
      I=40
  280 CONTINUE
C           READ NAME ETC.
      READ (IFILE,870) NAMELK(I),NLOOK(I),LKOLK(I),DHLOOK(I),LOOKFL(I)
      IF (IREAD.EQ.0) PRINT 880, NAMELK(I),NLOOK(I),LKOLK(I),DHLOOK(I),L
     1OOKFL(I)
      IF (NAMELK(I).NE.DELETE) GO TO 290
      I=0
      NLOOKS=I
      GO TO 270
  290 CONTINUE
      IF (NLOOK(I).EQ.0) GO TO 340
C           CHECK TO SEE IF MINERAL IS ALREADY IN THE LIST
      IF (I.LE.1) GO TO 310
      L=I-1
      DO 300 N=1,L
      IF (NAMELK(I).NE.NAMELK(N)) GO TO 300
      NLOOK(N)=NLOOK(I)
      LKOLK(N)=LKOLK(I)
      DHLOOK(N)=DHLOOK(I)
      LOOKFL(N)=LOOKFL(I)
      I=I-1
      GO TO 320
  300 CONTINUE                                                          B 2640
  310 CONTINUE                                                          B 2650
      N=I                                                               B 2660
      NLOOKS=I                                                          B 2670
C           N IS THE NUMBER FOR THE MINERAL BEING READ.                 B 2680
  320 CONTINUE                                                          B 2690
C           READ COEFFICIENTS                                           B 2700
      K=NLOOK(N)                                                        B 2710
      READ (IFILE,550) (LLOOK(N,J),CLOOK(N,J),J=1,K)                    B 2720
      IF (IREAD.EQ.0) PRINT 560, (LLOOK(N,J),CLOOK(N,J),J=1,K)          B 2730
C           READ ANALYTIC EXPRESSION                                    B 2740
      IF (LOOKFL(N).EQ.0) GO TO 330                                     B 2750
      READ (IFILE,570) (ALOOK(N,J),J=1,5)                               B 2760
      IF (IREAD.EQ.0) PRINT 580, (ALOOK(N,J),J=1,5)                     B 2770
  330 CONTINUE                                                          B 2780
      GO TO 270                                                         B 2790
  340 CONTINUE                                                          B 2800
      NLKS=NLOOKS                                                       B 2810
      CALL CHKLK                                                        B 2820
      ISUB(9)=1                                                         B 2830
      GO TO 40                                                          B 2840
C                                                                       B 2850
C           READ LISTS FOR SUMS OF SPECIES                              B 2860
C                                                                       B 2870
  350 CONTINUE                                                          B 2880
      PRINT 890                                                         B 2890
      I=NSMS                                                            B 2900
  360 CONTINUE                                                          B 2910
      I=I+1                                                             B 2920
      READ (IFILE,900) SUNAME(I),K                                      B 2930
      IF (IREAD.EQ.0) PRINT 910, SUNAME(I),K                            B 2940
      IF (SUNAME(I).NE.DELETE) GO TO 370                                B 2950
      I=0                                                               B 2960
      NSUMS=0                                                           B 2970
      GO TO 360                                                         B 2980
  370 CONTINUE                                                          B 2990
      IF (K.EQ.0) GO TO 380                                             B 3000
      NSUM(I)=K                                                         B 3010
      NSUMS=I                                                           B 3020
      READ (IFILE,920) (LSUM(I,J),J=1,K)                                B 3030
      IF (IREAD.EQ.0) PRINT 930, (LSUM(I,J),J=1,K)                      B 3040
      GO TO 360                                                         B 3050
  380 CONTINUE                                                          B 3060
      NSMS=NSUMS                                                        B 3070
      ISUB(10)=1                                                        B 3080
      GO TO 40                                                          B 3090
C                                                                       B 3100
C           READ SPECIES TO ADJUST FOR ELECTRICAL NEUTRALITY            B 3110
C                                                                       B 3120
  390 CONTINUE                                                          B 3130
      PRINT 940                                                         B 3140
      READ 950, LPOS,LNEG                                               B 3150
      PRINT 960, LPOS,LNEG                                              B 3160
      ISUB(11)=1                                                        B 3170
      GO TO 40                                                          B 3180
C                                                                       B 3190
C           END DATA ENTRY FOR THIS SIMULATION                          B 3200
C                                                                       B 3210
  400 CONTINUE                                                          B 3220
      IF (IREAD.EQ.1) RETURN                                            B 3230
      IF (IERR.GT.O) STOP
      IF (IOPT(4).GT.O.AND.ISUB(1).EQ.O) IERR=1                         B 3240
      IF (IOPT(3).GT.O.AND.IOPT(3).LT.5.AND.ISUB(5).EQ.O) IERR=5        B 3250
      IF (IOPT(3).GE.3.AND.IOPT(3).LT.5.AND.ISUB(4).EQ.O) IERR=4        B 3260
      IF (IOPT(3).EQ.5.AND.ISUB(2).EQ.O) IERR=2                         B 3270
      IF (IOPT(3).EQ.6.AND.ISUB(2).EQ.O) IERR=2                         B 3280
      IF (IOPT(3).EQ.6.AND.ISUB(4).EQ.O) IERR=4                         B 3290
      IF (IOPT(2).EQ.2.AND.ISUB(11).EQ.O) IERR=11                       B 3300
      IF (IERR.EQ.O) RETURN                                             B 3310
      PRINT 970, SUBS(IERR)                                             B 3320
      IF (IOPT(7).EQ.O) GO TO 10                                        B 3330
  410 CONTINUE                                                          B 3340
      STOP                                                              B 3350
C                                                                       B 3360
  420 FORMAT (20A4)                                                     B 3370
  430 FORMAT (10I1,I2,I2,6X,F10.5)                                      B 3380
  440 FORMAT (1H1,20A4)                                                 B 3390
  450 FORMAT (1X,10I1,I2,I2,6X,F10.5)                                   B 3400
  460 FORMAT (10X,'DATA READ FROM DISK'/)                               B 3410
  470 FORMAT (A8,1X,I1)                                                 B 3420
  480 FORMAT (1X,'** ',A8,' **  INPUT UNKNOWN')                         B 3430
  490 FORMAT (1X,'TEMP')                                                B 3440
  500 FORMAT (8F10.1)                                                   B 3450
  510 FORMAT (1X,8G10.3)                                                B 3460
  520 FORMAT (1X,'MINERALS')                                            B 3470
  530 FORMAT (A8,2X,I2,3X,3F10.2,5X,I1,9X,F10.3)                        B 3480
  540 FORMAT (1X,A8,2X,I2,3X,3G10.3,5X,I1,9X,F10.3)                     B 3490
  550 FORMAT ((5(I4,F11.3)))                                            B 3500
  560 FORMAT ((1X,5(I4,G11.3)))                                         B 3510
  570 FORMAT (5E12.5)                                                   B 3520
  580 FORMAT (1X,1P5E12.4)                                              B 3530
  590 FORMAT (1X,'SOLUTION ',I1)                                        B 3540
  600 FORMAT (20A4)                                                     B 3550
  610 FORMAT (1X,20A4)                                                  B 3560
  620 FORMAT (I2,I3,I2,3X,4F10.0)                                       B 3570
  630 FORMAT (1X,I2,I3,I2,3X,4G10.3)                                    B 3580
  640 FORMAT ((5(I4,D11.3)))                                            B 3590
  650 FORMAT ((1X,5(I4,1PD11.3)))                                       B 3600
  660 FORMAT (1X,'REACTION')                                            B 3610
  670 FORMAT ((4(I4,2F8.3)))                                            B 3620
  680 FORMAT ((1X,4(I4,2F8.3)))                                         B 3630
  690 FORMAT (1X,'STEPS')                                               B 3640
  700 FORMAT (8F10.3)                                                   B 3650
  710 FORMAT (1X,8G10.3)                                                B 3660
  720 FORMAT (1X,'ELEMENTS')                                            B 3670
  730 FORMAT (A8,2X,I2,3X,F10.0)                                        B 3680
  740 FORMAT (1X,A8,2X,I2,3X,F10.0)                                     B 3690
  750 FORMAT (1X,I4,2X,A8,5X,A8,' INDEX NUMBER IS OUT OF RANGE.'//1X,'CAB 3700
     1LCULATION TERMINATED.')                                           B 3710
  760 FORMAT (1X,'SPECIES')                                             B 3720
  770 FORMAT (I3)                                                       B 3730
  780 FORMAT (1X,I3)                                                    B 3740
  790 FORMAT (A8,2X,I3,I1,I1,6F10.3)                                    B 3750
  800 FORMAT (1X,A8,2X,I3,I1,I1,6F10.3)                                 B 3760
  810 FORMAT (2F10.3,5E12.5)                                            B 3770
  820 FORMAT (1X,2F10.3,5G12.5)                                         B 3780
  830 FORMAT (6(I3,F7.3))                                               B 3790
  840 FORMAT ((1X,6(I3,F7.3)))                                          B 3800
  850 FORMAT (1X,'LOOK MIN')                                            B 3810
  860 FORMAT (1X,'***** LOOK MIN ARRAY ALREADY HAS 40 MINERALS. *****') B 3820
                                                                        B 3830
  870 FORMAT (A8,2X,I2,13X,2F10.2,5X,I1)
  880 FORMAT (1X,A8,2X,I2,13X,2G10.3,5X,I1)
  890 FORMAT (1X,'SUMS')
  900 FORMAT (A8,2X,I2)
  910 FORMAT (1X,A8,2X,I2)
  920 FORMAT (20I4)
  930 FORMAT (1X,20I4)
  940 FORMAT (1X,'NEUTRAL')
  950 FORMAT (2I5)
  960 FORMAT (1X,2I5)
  970 FORMAT (//1X,14('*')/1X,'TERMINAL ERROR  INPUT LACKED ',A8,' CARDS
     1'/1X,14('*'))
      END
      SUBROUTINE MINCON
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
C          LOOP ON NUMBER OF MINERALS
      DO 100 I=1,NRMINS
      K=NMINO(I)
      ICOMP=0
      NONMAS=0
C          LOOP ON INDIVIDUAL MINERAL
      DO 90 J=1,K
      IF (LMINO(I,J).GT.MAXT) GO TO 40
      IF (ICOMP.EQ 0) GO TO 20
C          CHECK TO SEE IF COMPONENT IS ALREADY IN LIST
      DO 10 I1=1,ICOMP
      IF (LMIN(I,I1).EQ.LMINO(I,J)) GO TO 30
   10 CONTINUE
   20 CONTINUE
C           COMPONENT NOT IN LIST
      ICOMP=ICOMP+1
      LMIN(I,ICOMP)=LMINO(I,J)
      CMIN(I,ICOMP)=CMINO(I,J)
      GO TO 90
C         COMPONENT ALREADY IN LIST
   30 CONTINUE
      CMIN(I,I1)=CMIN(I,I1)+CMINO(I,J)
      GO TO 90
C             COMPONENT MUST BE REDUCED TO MASTER SPECIES
   40 CONTINUE
      J1=LMINO(I,J)
      K1=NSP(J1)
      NONMAS=NONMAS+1
      LMCON(I,NONMAS)=J1
      CMCON(I,NONMAS)=-CMINO(I,J)
C             LOOP THROUGH MASTER SPECIES OF NON-MASTER SPECIES COMPONENT
      DO 80 I1=1,K1
      IF (ICOMP.EQ.0) GO TO 60
      DO 50 L1=1,ICOMP
      IF (LSP(J1,I1).EQ.LMIN(I,L1)) GO TO 70
   50 CONTINUE
C             MASTER SPECIES NOT IN LIST
   60 CONTINUE
      ICOMP=ICOMP+1
      LMIN(I,ICOMP)=LSP(J1,I1)
      CMIN(I,ICOMP)=CMINO(I,J)*CSP(J1,I1)
      GO TO 80
C             MASTER SPECIES IN LIST
   70 CONTINUE
      CMIN(I,L1)=CMIN(I,L1)+CMINO(I,J)*CSP(J1,I1)
   80 CONTINUE
C             END LOOP MASTER SPECIES OF NON MASTER SPECIES COMPONENT
   90 CONTINUE
      NMIN(I)=ICOMP
      NMCON(I)=NONMAS
C             END LOOP ON SINGLE MINERAL
  100 CONTINUE
C             END ALL MINERALS
      RETURN
      END
      SUBROUTINE PICK1
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      REAL*8 SUNAME(10)
      COMMON /NEUT/ SUNAME,DNEUT,NSUM(10),NSUMS,LSUM(10,50),LPOS,LNEG
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C
C          THIS SUBROUTINE CHOOSES THE MODEL FOR THE INITIAL SOLUTIONS
C
      DZOFF=0D0
      IIN(1)=1
      IIN(2)=0
      IIN(3)=0
      NMINS=0
      IFE=1
      ILE=1
      IF (IESPEC.EQ.1) GO TO 10
      IIN(1)=0
      IFE=0
      ILE=0
   10 CONTINUE
C          CHECK ALKALINITY TOTAL
      DALKT=0D0
      IASPEC=IALK(ISOL)
      IF (IASPEC.EQ.0) GO TO 30
      IF(TOTAL(ISOL,IASPEC).GT.0D0) GO TO 20
      PRINT 140
      STOP
   20 CONTINUE
      IF(IOPT(2).NE.1) GO TO 25
      PRINT 160
      STOP
   25 CONTINUE
      DALKT=TOTAL(ISOL,IASPEC)
      IF (IESPEC.EQ.0.OR.IESPEC.NE.IASPEC) GO TO 30
      PRINT 150
      STOP
   30 CONTINUE
      DNEUT=0.0
      IF (IESPEC.LT.4) GO TO 40
C          MAKE SURE NEUTRAL SPECIES .GT. 0
      DNEUT=TOT(IESPEC)
      IF (TOT(IESPEC).LE.0D0) TOT(IESPEC)=1D-3
   40 CONTINUE
      CALL INOUT
C          SET COUNTERS ON THE ARRAY
      IFTH=0
      ILTH=0
      IFT=ILE+1
      ILT=ILT
      IFM=0
      ILM=0
      NEQ=ILT
      NEQ1=NEQ+1
      RETURN
C      *****
      ENTRY PICK2
C      *****
C
C          THIS SUBROUTINE CHOOSES THE MODEL FOR THE REACTION SOLUTIONS
C
      IIN(1)=1
      IIN(2)=0
      IF (IOPT(5).GT.0) IIN(2)=1
      IIN(3)=0
      IESPEC=1
      IASPEC=0                                                          D 880
      NMINS=NRMINS                                                      D 890
C             ADD IN ANY MINERALS NOT INCLUDED IN TOTALS                 D 900
      IF (NMINS.EQ.0) GO TO 110                                         D 910
      TOT(3)=1D0                                                        D 920
      ICK=0                                                             D 930
      DO 50 I=1,NMINS                                                   D 940
      TOT(MAXT+I)=0D0                                                   D 950
   50 CONTINUE                                                          D 960
   55 CONTINUE                                                          D 970
C             CHECK TO MAKE SURE NECESSARY TOTALS > 0.                   D 980
      JCK=0                                                             D 990
      ICK=ICK+1                                                         D 1000
      DO 70 I=1,NMINS                                                   D 1010
      IF (IOPT(3).EQ.6.AND.I.EQ.1) GO TO 70                             D 1020
      K=NMIN(I)                                                         D 1030
C             IF TOTALS > 0 NEXT MINERAL                                 D 1040
      DO 60 J=1,K                                                       D 1050
      IF (LMIN(I,J).LT.4) GO TO 60                                      D 1060
      IF(TOT(LMIN(I,J)).GT.0D0) GO TO 60                                D 1070
      GO TO 65                                                          D 1080
   60 CONTINUE                                                          D 1090
      GO TO 70                                                          D 1100
   65 CONTINUE                                                          D 1110
C             SOME TOTAL <= 0.  IF ALL CMIN > 0 ADD MINERAL.             D 1120
      DO 75 J=1,K                                                       D 1130
      IF (LMIN(I,J).LT.4) GO TO 75                                      D 1140
      IF (CMIN(I,J).GT.0) GO TO 75                                      D 1150
      GO TO 85                                                          D 1160
   75 CONTINUE                                                          D 1170
      D=1D-6                                                            D 1180
C             ADD D OF MINERAL # I.                                      D 1190
   95 CONTINUE                                                          D 1200
      TOT(MAXT+I)=D                                                     D 1210
      THOR=THOR+THMIN(I)*D                                              D 1220
      DO 105 J=1,K                                                      D 1230
      K1=LMIN(I,J)                                                      D 1240
      IF(K1.LT.4)GO TO 105                                              D 1250
      TOT(K1)=TOT(K1)+D*CMIN(I,J)                                       D 1260
  105 CONTINUE                                                          D 1270
      GO TO 70                                                          D 1280
C             SOME TOTAL <= 0.  CHECK IF TOTALS <= 0 HAVE SAME SIGN FOR CMID 1290
   85 CONTINUE                                                          D 1300
      NCNEG=0                                                           D 1310
      NCPOS=0                                                           D 1320
      D=1D1                                                             D 1330
      DO 115 J=1,K                                                      D 1340
      K1=LMIN(I,J)                                                      D 1350
      D1=TOT(K1)                                                        D 1360
      IF (D1.LE.0D0) GO TO 125                                          D 1370
      IF (D1.LT.D) D=D1                                                 D 1380
      GO TO 115                                                         D 1390
  125 CONTINUE                                                          D 1400
      IF(CMIN(I,J).LE.0D0) NCNEG=1                                      D 1410
      IF(CMIN(I,J).GT.0D0) NCPOS=1                                      D 1420
  115 CONTINUE                                                          D 1430
      IF(NCNEG.GT.0.AND.NCPOS.GT.0) GO TO 135                           D 1440
      D=D/5D1                                                           D 1450
      IF(NCNEG.EQ.1) D=-D                                               D 1460
      GO TO 95                                                          D 1470
  135 CONTINUE                                                          D 1480
      JCK=1                                                             D 1490
   70 CONTINUE                                                          D 1500
      IF(JCK.EQ.0) GO TO 145                                            D 1510
      IF(ICK.LE.NMINS+1) GO TO 55                                       D 1520
      PRINT 155                                                         D 1530
  155 FORMAT(1H1,90('*')/'I HAD TROUBLE ADDING MINERALS SO THAT',       D 1540
     1       ' ALL THE NECESSARY ELEMENTS HAD POSITIVE CONCENTRATIONS.'/ D 1550
     2       'PLEASE ADJUST INITIAL CONCENTRATIONS TO SOME SMALL ',     D 1560
     3       'POSITIVE QUANTITY.'/90('*'))                              D 1570
      STOP                                                              D 1580
  145 CONTINUE                                                          D 1590
C             ADD ANY REACTION ELEMENTS IF IOPT(3)=6.                    D 1600
      IF (IOPT(3).NE.6) GO TO 100                                       D 1610
      DO 90 I=1,NCOMPS                                                  D 1620
      IF (TOT(LREAC(I)).GT.0D0) GO TO 90                                D 1630
      D=SIGN(1E-6,CREAC(I))                                             D 1640
      TOT(MAXT1)=D                                                      D 1650
      DO 80 J=1,NCOMPS                                                  D 1660
      THOR=THOR+CREAC(J)*THMEAN(J)*D                                    D 1670
      TOT(LREAC(J))=TOT(LREAC(J))+CREAC(J)*D                            D 1680
   80 CONTINUE                                                          D 1690
      GO TO 100                                                         D 1700
   90 CONTINUE                                                          D 1710
  100 CONTINUE                                                          D 1720
      TOT(1)=1D1**(-PH)                                                 D 1730
      TOT(2)=1D1**(-PE)                                                 D 1740
      TOT(3)=1D0                                                        D 1750
  110 CONTINUE                                                          D 1760
      CALL INOUT                                                        D 1770
C             SET COUNTERS FOR ARRAY                                     D 1780
      IFE=1                                                             D 1790
      ILE=1                                                             D 1800
      LAST=1                                                            D 1810
      IFTH=0                                                            D 1820
      ILTH=0                                                            D 1830
      IF (IIN(2).LE.0) GO TO 120                                        D 1840
      IFTH=2                                                            D 1850
      ILTH=2                                                            D 1860
      LAST=2                                                            D 1870
  120 CONTINUE                                                          D 1880
      IFT=LAST+1                                                        D 1890
      ILT=ILT                                                           D 1900
      IFM=0                                                             D 1910
      ILM=0                                                             D 1920
      NEQ=ILT                                                           D 1930
      IF (NMINS.EQ.0) GO TO 130                                         D 1940
      IFM=ILT+1                                                         D 1950
      ILM=ILT+NMINS                                                     D 1960
      NEQ=ILM                                                           D 1970
  130 CONTINUE                                                          D 1980
      NEQ1=NEQ+1                                                        D 1990
      RETURN                                                            D 2000
C                                                                        D 2010
  140 FORMAT (1X,'CARBON WAS SPECIFIED AS ALKALINITY BUT WAS LESS ','THAD 2020
     1N OR EQUAL 0.0.'/1X,'CALCULATIONS TERMINATED')                    D 2030
  150 FORMAT (1X,'ALKALINITY SPECIES CAN NOT BE THE SAME AS THE ','NEUTRD 2040
     1AL SPECIES'/1X,'CALCULATIONS TERMINATED')                         D 2050
  160 FORMAT(1H1,90('*')//1X,'IT IS THEORETICALLY IMPOSSIBLE ',         D 2060
     1      'TO FIX THE ALKALINITY AND STILL FIND ELECTRICAL ',         D 2070
     2      'NEUTRALITY BY ADJUSTING PH.'/1X,'IF ALKALINITY ',
     3      'IS TO BE INPUT, IOPT(2) CAN NOT BE EQUAL TO 1.'/
     4      /1X,90('*'))
      END
      SUBROUTINE INOUT
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
C
C           DETERMINE TOTALS TO BE INCLUDED AS EQUATIONS IN MATRIX.
C
      DO 10 I=4,MAXT
      IIN(I)=0
      IF (TOT(I).LE.0.0D0) GO TO 10
      IIN(I)=1
   10 CONTINUE
      LAST=0
      LASTT=0
      DO 20 I=1,MAXT
      IF (IIN(I).EQ.0) GO TO 20
      LAST=LAST+1
      IIN(I)=LAST
      LASTT=I
      IOUT(LAST)=I
   20 CONTINUE
      ILT=LAST
C           PICK SPECIES TO BE INCLUDED
      IF (LASTT.LT.4) LASTT=4
      SFLAG(1)=1
      SFLAG(2)=1
      SFLAG(3)=1
      DO 30 I=4,MAXT
      SFLAG(I)=0
      IF (IIN(I).GT.0) SFLAG(I)=1
   30 CONTINUE
      DO 50 I=MAXT1,MAXS
      SFLAG(I)=0
      K=NSP(I)
      IF (K.EQ.0) GO TO 50
      DO 40 J=1,K                                                       E 570
      IF (SFLAG(LSP(I,J)).LE.O) GO TO 50                                E 580
   40 CONTINUE                                                          E 590
      SFLAG(I)=1                                                        E 600
      LASTS=I                                                           E 610
   50 CONTINUE                                                          E 620
C             ZERO ARRAY AR                                              E 630
      DO 70 I=1,MAXEQ                                                   E 640
      DO 60 J=1,MAXEQ                                                   E 650
      AR(I,J)=ODO                                                       E 660
   60 CONTINUE                                                          E 670
   70 CONTINUE                                                          E 680
C             PUT MINERAL COEFFICIENTS INTO FULL ARRAY                   E 690
      IF (NMINS.LE.O) GO TO 120                                         E 700
      DO 90 I=1,NMINS                                                   E 710
      K=NMIN(I)                                                         E 720
      L=MAXT+I                                                          E 730
      DO 80 J=1,K                                                       E 740
      K1=LMIN(I,J)                                                      E 750
      AR(K1,L)=-CMIN(I,J)                                               E 760
      AR(L,K1)=CMIN(I,J)                                                E 770
   80 CONTINUE                                                          E 780
      AR(1,L)=ODO                                                       E 790
      AR(2,L)=-THMIN(I)                                                 E 800
   90 CONTINUE                                                          E 810
      IF (IOPT(3).NE.6) GO TO 120                                       E 820
C             ADD REACTION TO EQUILBRATE WITH MINERAL # 1.               E 830
      L=MAXT+1                                                          E 840
      DO 100 I=1,MAXT                                                   E 850
      AR(I,L)=ODO                                                       E 860
  100 CONTINUE                                                          E 870
      DO 110 I=1,NCOMPS                                                 E 880
      J=LREAC(I)                                                        E 890
      AR(J,L)=AR(J,L)-CREAC(I)                                          E 900
      AR(2,L)=AR(2,L)-CREAC(I)*THMEAN(I)                                E 910
  110 CONTINUE                                                          E 920
  120 CONTINUE                                                          E 930
      RETURN                                                            E 940
      END                                                               E 950
      SUBROUTINE KTEMP                                                  F  10
      IMPLICIT REAL*8(D),INTEGER*2(I-N)                                 F  20
      REAL*8 S1,S2,S3,C1                                                F  30
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,         F  40
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL                 F  50
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),          F  60
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),         F  70
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),               F  80
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),      F  90
     4       DALKT,DALKS,DIFFZ(2),DZOFF                                 F 100
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA                         F 110
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),         F 120
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),                   F 130
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),        F 140
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),             F 150
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),       F 160
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),                      F 170
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)            F 180
      INTEGER*2 GFLAG,SFLAG                                             F 190
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),          F 200
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,           F 210
     2     IFTH,ILTH,IFT,ILT,IFM,ILM,MEQ,NEQ1,IESPEC,ISOLV(2),
     3     NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4     LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5     NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6     MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      DATA C/2.302585092/,R/1.98719E-3/
      REAL*8 NAMELK
      REAL*4 LKLOOK,LKOLK
      COMMON /LOOK/ NAMELK(40),LKOLK(40),LKLOOK(40),DHLOOK(40),
     1     ALOOK(40,10),CLOOK(40,10),LLOOK(40,10),NLOOK(40),
     2     LOOKFL(40),NLOOKS
      COMMON /OFFSET/ SIMIN(20)
C
C          COMPUTE TEMPERATURE DEPENDENCE OF A AND B FOR DEBYE-HUCKEL
C
      S1=374.11-TC
      S2=S1**0.33333333
      S3=1.0+0.1342489*S2-3.946263E-03*S1
      S3=S3/(3.1975-0.3151548*S2-1.203374E-03*S1+7.48908E-13*S1**4.0)
      S3=DSQRT(S3)
      IF (TK.LT.373.16) GO TO 10
      C1=5321.0/TK+233.76-TK*(TK*(8.292E-07*TK-1.417E-03)+0.9297)
      GO TO 20
   10 C1=87.74-TC*(TC*(1.41E-06*TC-9.398E-04)+0.4008)
   20 CONTINUE
      C1=DSQRT(C1*TK)
      A=1824600.0*S3/C1**3.0
      B=50.29*S3/C1
C
C          COMPUTE VANT HOFF CONSTANTS
C
      C1=(298.16-TK)/(298.16*TK*C*R)
      DO 30 I=1,LASTS
      IF (SFLAG(I).EQ.0) GO TO 30
      IF (KFLAG(I).EQ.1) LKSP(I)=ASP(I,1)+(ASP(I,2)+ASP(I,4)*TK)*TK+(ASP
     1(I,3)+ASP(I,5)/TK)/TK
      IF (KFLAG(I).EQ.0) LKSP(I)=LKTOSP(I)-DHSP(I)*C1
   30 CONTINUE
      IF (NLOOKS.EQ.0) GO TO 50
      DO 40 I=1,NLOOKS
      IF (LOOKFL(I).EQ.0) LKLOOK(I)=LKOLK(I)-DHLOOK(I)*C1
      IF (LOOKFL(I).EQ.1) LKLOOK(I)=ALOOK(I,1)+(ALOOK(I,2)+ALOOK(I,4)*TK
     1)*TK+(ALOOK(I,3)+ALOOK(I,5)/TK)/TK
   40 CONTINUE
   50 CONTINUE
      TKEEP=TC
      RETURN
C      *****
      ENTRY KMIN
C      *****
      IF (NMINS.EQ.0) GO TO 80
      DO 70 I=1,NMINS
      IF (MFLAG(I).EQ.0) LKMINO(I)=LKTOM(I)-DHMIN(I)*C1
      IF (MFLAG(I).EQ.1) LKMINO(I)=AMIN(I,1)+(AMIN(I,2)+AMIN(I,4)*TK)*TK
     1+(AMIN(I,3)+AMIN(I,5)/TK)/TK
C          CONVERT K TO MASTER SPECIES
      LKMIN(I)=LKMINO(I)+SIMIN(I)
      IF (NMCON(I).EQ.0) GO TO 70
      K=NMCON(I)
      DO 60 J=1,K
      LKMIN(I)=CMCON(I,J)*LKSP(LMCON(I,J))+LKMIN(I)                    F 820
   60 CONTINUE                                                          F 830
   70 CONTINUE                                                          F 840
   80 CONTINUE                                                          F 850
      RETURN                                                            F 860
      END                                                               F 870
      SUBROUTINE SET                                                    G 10
      IMPLICIT REAL*8(D),INTEGER*2(I-N)                                 G 20
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,         G 30
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL                 G 40
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),          G 50
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),         G 60
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),               G 70
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),      G 80
     4       DALKT,DALKS,DIFFZ(2),DZOFF                                 G 90
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA                         G 100
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),         G 110
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),                   G 120
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),        G 130
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),             G 140
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(5C),       G 150
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),                      G 160
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)            G 170
      INTEGER*2 GFLAG,SFLAG                                             G 180
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),          G 190
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,           G 200
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),        G 210
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),      G 220
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,       G 230
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,        G 240
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)             G 250
      LA(1)=DLOG10(TOT(1))                                              G 260
      LA(2)=DLOG10(TOT(2))                                              G 270
      LA(3)=0.0D0                                                       G 280
      M(1)=1D1**(LA(1))                                                 G 290
      DO 10 I=4,LASTT                                                   G 300
      IF (IIN(I).LE.0) GO TO 10                                         G 310
      IF (TOT(I).LE.0.0D0) TOT(I)=1D-10                                 G 320
      M(I)=0.1D0*TOT(I)                                                 G 330
      LA(I)=DLOG10(M(I))                                                G 340
   10 CONTINUE                                                          G 350
      DO 20 I=MAXT1,LASTS                                               G 360
      M(I)=0.0D0                                                        G 370
   20 CONTINUE                                                          G 380
      RETURN                                                            G 390
      END                                                               G 400
      SUBROUTINE STEP                                                   H 10
      IMPLICIT REAL*8(D),INTEGER*2(I-N)                                 H 20
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,         H 30
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL                 H 40
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),          H 50
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),         H 60
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),               H 70
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),      H 80
     4       DALKT,DALKS,DIFFZ(2),DZOFF                                 H 90
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA                         H 100
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),         H 110
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),                   H 120
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),        H 130
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),             H 140
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      IF (IOPT(3).EQ.0) GO TO 120
      I=IOPT(3)
      PRINT 140, ISTEP
      GO TO (10,30,50,60,100,100), I
      GO TO 100
C          MIX SOLUTION 1 WITH SOLUTION 2
   10 CONTINUE
      X1=XSTEP(ISTEP)
      X2=1.0-X1
      DO 20 I=1,MAXT
      TOT(I)=X1*TOTAL(1,I)+X2*TOTAL(2,I)
   20 CONTINUE
      THOR=TH(1)*X1+TH(2)*X2
      TC=X1*TEMP(1)+X2*TEMP(2)
      DZOFF=X1*DIFFZ(1)+X2*DIFFZ(2)
      PRINT 150, X1,X2
      GO TO 120
C          TITRATE
   30 CONTINUE
      X1=XSTEP(ISTEP)
      VTOT=VO+X1
      DO 40 I=1,MAXT
      TOT(I)=(TOTAL(1,I)*VO+TOTAL(2,I)*X1)/VTOT
   40 CONTINUE
      TC=(TEMP(1)*VO+TEMP(2)*X1)/VTOT
      THOR=(TH(1)*VO+TH(2)*X1)/VTOT
      DZOFF=(DIFFZ(1)*VO+DIFFZ(2)*X1)/VTOT
      PRINT 160, X1
      GO TO 120
C          ADD REACTION IN INCREMENTS
   50 CONTINUE
      X1=XSTEP(ISTEP)
      GO TO 70
C          ADD REACTION LINEARLY
   60 CONTINUE
      X1=(ISTEP*XSTEP(1))/NSTEPS
   70 CONTINUE
      DZOFF=DIFFZ(1)
      DO 80 I=1,MAXT
      TOT(I)=TOTAL(1,I)
   80 CONTINUE
      DO 90 I=1,NCOMPS
      K=LREAC(I)
      IF (K.EQ.0) DZOFF=DIFFZ(1)+X1*CREAC(I)
      IF (K.LT.4.OR.K.GT.MAXT) GO TO 90
      TOT(K)=TOT(K)+X1*CREAC(I)
   90 CONTINUE
      THOR=TH(1)+THREAC*X1
      TC=TEMP(1)
      IF (ISTEP.GT.1) TOT(1)=1D1**LA(1)
      PRINT 170, X1
      CALL PREAC
      GO TO 120
C           FOLLOW PHASE BOUNDARIES ONLY
  100 CONTINUE
      DO 110 I=1,MAXT
      TOT(I)=TOTAL(1,I)
  110 CONTINUE
      THOR=TH(1)
      TC=TEMP(1)
      DZOFF=DIFFZ(1)
      PRINT 180
  120 CONTINUE
C           TEMPERATURE
      IF (IOPT(4).EQ.0) GO TO 130
      IF (IOPT(4).EQ.1) TC=TSTEP(1)
      IF (IOPT(4).EQ.2) TC=(ISTEP*(TSTEP(2)-TSTEP(1)))/NSTEPS+TSTEP(1)
      IF (IOPT(4).EQ.3) TC=TSTEP(ISTEP)
      PRINT 190, TC
  130 CONTINUE
      TK=TC+273.16
      RETURN
C
  140 FORMAT (1H1,'STEP NUMBER',I3,/1H0,14('-'))
  150 FORMAT (1H0,24X,F10.3,' = FRACTION OF SOLUTION 1.',5X,F10.3,' = FR
     1ACTION OF SOLUTION 2.'//)
  160 FORMAT (1H0,24X,F10.3,' VOLUME UNITS OF SOLUTION 2 HAVE BEEN ','AD
     1DED.'//)
  170 FORMAT (1H0,24X,1PD10.3,' MOLES OF REACTION HAVE BEEN ADDED.'//)
  180 FORMAT (//)
  190 FORMAT (25X,F10.2,' = NEW TEMPERATURE (C).'//)
      END
      SUBROUTINE MODEL
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1        SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2        IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3        NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4        LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5        NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6        MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      CALL SET
      ITER=0
   10 CONTINUE
      ITER=ITER+1
      CALL GAMMA
      CALL ZEROAR
      CALL AQMOD
      CALL CHECK(&30,&20)
      CALL SOLVE
   20 CONTINUE
      CALL RESET
      GO TO 10
   30 CONTINUE
      RETURN
      END
      SUBROUTINE GAMMA
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 SUM,MUHALF,AMU,BMU,CMU,ZCHRG
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
C          CALCULATE IONIC STRENGTH
      DOLDMU=MU
      SUM=M(1)
      MU=M(1)
      DO 10 I=4,LASTS
      IF (SFLAG(I).EQ.0) GO TO 10
      SUM=SUM+M(I)
      MU=MU+M(I)*ZSP(I)*ZSP(I)
   10 CONTINUE
      IF (ITER.EQ.1) GO TO 20
      IF (SUM-DSUM.LT.1D0) GO TO 20
      SUM=DSUM+1D0
   20 CONTINUE
      DSUM=SUM
      MU=MU*0.5
      MU=DMIN1(MU,1D1)
      IF (ITER.EQ.1) GO TO 30
      IF (DABS(DOLDMU-MU).LE.0.75D0) GO TO 30
      MU=DOLDMU+((MU-DOLDMU)/DABS(MU-DOLDMU))*0.5D0
   30 CONTINUE
      MUHALF=DSQRT(MU)
C          ACTIVITY OF WATER
      AH2O=1.0-SUM*0.017
      IF (SUM.GT.40.0D0) AH2O=0.32
      LA(3)=ALOG10(AH2O)
      TOT(3)=AH2O
C          CALCULATE ACTIVITY COEFFICIENTS
      AMU=-A*MUHALF
      BMU=B*MUHALF
      CMU=-A*(MUHALF/(1.0+MUHALF)-0.3*MU)
      ZCHRG=0.1*MU
      LG(1)=AMU/(1.0+DHA(1)*BMU)
      IF (IOPT(6).EQ.1) LG(1)=CMU
      LG(2)=0.0D0
      LG(3)=0.0D0
      DO 70 I=4,LASTS
      IF (SFLAG(I).EQ.0) GO TO 70
      IF (ZSP(I).EQ.0.0) GO TO 40
      IF (GFLAG(I).EQ.1) GO TO 50
      IF(DHA(I).LE.0D0) GO TO 60
      IF (IOPT(6).EQ.1) GO TO 60
      LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+DHA(I)*BMU)
      GO TO 70
   40 LG(I)=ZCHRG
      GO TO 70
   50 LG(I)=AMU*ZSP(I)*ZSP(I)/(1.0+ADHSP(I,1)*BMU)+ADHSP(I,2)*MU
      GO TO 70
   60 LG(I)=CMU*ZSP(I)*ZSP(I)
   70 CONTINUE
C           LG FOR CARBONIC ACID
      RETURN
      END
      SUBROUTINE AQMOD
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1        LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1        SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2        AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3        MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4        DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1        DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2        TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3        DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4        LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5        TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6        THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1        SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2        IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3        NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4        LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5        NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6        MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      REAL*8 UNDER
      REAL*8 ANO3,A1,B1,C1
      DIMENSION DM2(30)
      ELECT=0.0D0
      THSOLN=0.0D0
      DALKS=0D0
C           CATIONS AND ANIONS
      DO 80 IZ=1,2
      DO 10 I=1,MAXT
      DM2(I)=0D0
   10 CONTINUE
C           CALCULATE MOLALITIES WITH NEW GAMMAS, OLD ACTIVITIES.
      DO 40 I=1,LASTS
      IF (SFLAG(I).EQ.0) GO TO 40
      K=NSP(I)
      DM=LKSP(I)-LG(I)
      DO 20 J=1,K
      DM=DM+LA(LSP(I,J))*CSP(I,J)
   20 CONTINUE
```

```
      LM(I)=DM
      M(I)=UNDER(DM)
      IF (M(I).GT.1D1.AND.IOPT(8).GT.0.AND.I.NE.2) PRINT 150, I,LM(I)
      IF (M(I).EQ.0D0) GO TO 40
C            SUM MOLALITIES FOR EACH MAJOR SPECIES
      DO 30 I1=1,K
      DM=M(I)*CSP(I,I1)
      K2=LSP(I,I1)
      IF (K2.LT.4) GO TO 30
      AR(K2,K2)=AR(K2,K2)+DM
      IF (CSP(I,I1).GT.1D0) DM2(K2)=DM2(K2)+DM
   30 CONTINUE
   40 CONTINUE
C            CALCULATE NEW ACTIVITIES
      DO 70 K=4,LASTT
      IF (IIN(K).EQ.0) GO TO 70
      IF (IESPEC.EQ.K) GO TO 60
      IF (IASPEC.EQ.K) GO TO 60
      IF (ZSP(K).LE.0.0.AND.IZ.EQ.1) GO TO 60
      IF (ZSP(K).GT.0.0.AND.IZ.EQ.2) GO TO 60
      IF (AR(K,K).LE.0D0) AR(K,K)=1D-35
      IF (DM2(K)/AR(K,K).LT.1D-6) GO TO 50
      IF(AR(K,K)/TOT(K).GT.1D3) GO TO 50
      A1=DM2(K)
      B1=AR(K,K)-A1
      C1=TOT(K)
      AN03=B1-DSQRT(B1*B1+4D0*A1*C1)
      IF(AN03.GE.0D0) AN03=-1D-6
      LA(K)=LA(K)+1.00D0*(DLOG10(-AN03)-DLOG10(2D0*A1))
      GO TO 60
   50 CONTINUE
      LA(K)=LA(K)+1.00D0*(DLOG10(TOT(K))-DLOG10(AR(K,K)))
   60 CONTINUE
      AR(K,K)=0D0
   70 CONTINUE
   80 CONTINUE
      ZSP(2)=0.0
      DO 120 I=1,LASTS
      IF (SFLAG(I).EQ.0) GO TO 120
      ICK=0
      K=NSP(I)
      DM=LKSP(I)-LG(I)
C            CALCULATE MOLALITY
      DO 90 J=1,K
      DM=DM+LA(LSP(I,J))*CSP(I,J)
      IF(LSP(I,J).GT.3) ICK=1
   90 CONTINUE
      LM(I)=DM
      M(I)=UNDER(DM)
      IF(ICK.GT.0.AND.DM.LT.-25.0D0) M(I)=0D0
      IF (M(I).EQ.0D0) GO TO 120
C            SUM MOLALITY INTO PROPER ROWS AND COLUMNS
      DO 110 I1=1,K
      DM=M(I)*CSP(I,I1)
      K2=LSP(I,I1)
C            MASS BALANCE
      DO 100 J1=1,K
      K1=LSP(I,J1)
      IF (K1.LT.4) GO TO 100
      AR(K1,K2)=AR(K1,K2)+DM
```

```
  100 CONTINUE
C           ELECTRICAL BALANCE
      AR(1,K2)=AR(1,K2)+DM*ZSP(I)
C           THOR BALANCE
      AR(2,K2)=AR(2,K2)+DM*THSP(I)
C           ALKALINITY EQUATION
      AR(3,K2)=AR(3,K2)+DM*ALKSP(I)
  110 CONTINUE
      THSOLN=THSOLN+M(I)*THSP(I)
      ELECT=ELECT+M(I)*ZSP(I)
      DALKS=DALKS+M(I)*ALKSP(I)
  120 CONTINUE
      ZSP(2)=-1.0
C      *****
      ENTRY SI
C      *****
      IF (NMINS.EQ.0) RETURN
      DO 140 I=1,NMINS
      J=MAXT+I
      K=NMIN(I)
C           CALCULATE INVERSE SATURATION INDEX
      DSI=LKMIN(I)
      DO 130 I1=1,K
      DSI=DSI-LA(LMIN(I,I1))*CMIN(I,I1)
  130 CONTINUE
      CR(J)=DSI*DLOG(1D1)
  140 CONTINUE
      RETURN
C
  150 FORMAT (1X,'SPECIES NUMBER ',I3,' IS LARGE.  LM = ',D12.4)
      END
      SUBROUTINE CHECK(*,*)
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      REAL*8 ECLOSE,THCLOS,TCLOSE,MCLOSE
      DATA ECLOSE,TCLOSE,THCLOS,MCLOSE /1D-11,1D-7,1D-7,1D-5/
      ICHECK=0
      JCHECK=0
      IF (ITER.EQ.1) DAH2O=1DO
      D1=DAH2O/TOT(3)
      IF (D1.LT.O.8DO.OR.D1.GT.1.2DO) JCHECK=1
      DAH2O=TOT(3)
      IF (ITER.EQ.1) DOLDMU=O.1DO
      IF (DABS(MU-DOLDMU).GT.O.5) JCHECK=1
      DOLDMU=MU
      CR(1)=DZOFF-ELECT
      CR(2)=THOR-THSOLN
      CR(3)=DALKT-DALKS
C           CALCULATE MASS BALANCE
      THTOT = DABS(THOR)
      DO 10 I=4,LASTT
      IF (IIN(I).LE.O) GO TO 10
      CR(I)=TOT(I)-AR(I,I)
      THTOT=ABS(THSP(I))
   10 CONTINUE
C           CHECK ELECTRICAL BALANCE
      DCHECK=1D1**(DABS(PH-7DO))*ECLOSE
      IF (IESPEC.GT.O.AND.DABS(CR(1)).GT.DCHECK) ICHECK=1
C           CHECK THOR BALANCE
      IF (IIN(2).GT.O.AND.DABS(CR(2)).GT.THCLOS*THTOT) ICHECK=1
C           CHECK ALKALINITY
      IF (IASPEC.GT.O.AND.DABS(CR(3)).GT.TCLOSE*DALKT) ICHECK=1
C           CHECK MINERAL EQUILIBRIA
      DC=ODO
      IF (NMINS.EQ.O) GO TO 40
      DO 30 I=1,NMINS
      K=MAXT+I
      DC=DMAX1(DC,DABS(CR(K)))
      IF (DABS(CR(K)).GT.MCLOSE) ICHECK=1
   30 CONTINUE
   40 CONTINUE
C           CHECK MASS BALANCES
      IF(ITER.LE.1) DC=O.2DO
      IF(ITER.LE.1) DCC=O.2DO
      IF(DC.EQ.ODO) DC=O.2DO
      DCC=DMIN1(DCC,DC)
      DC=1D1**(-ITER/2D1)
      DC=DMAX1(DC,1D-5)
      DCC=DMIN1(DCC,DC)
      DC=DCC
      DO 20 I=4,LASTT
      IF (IIN(I).LE.O) GO TO 20
      IF (I.EQ.IESPEC) GO TO 20
      IF (I.EQ.IASPEC) GO TO 20
      IF (DABS(CR(I)).GT.TCLOSE*TOT(I)) ICHECK=1
      DT=AR(I,I)/TOT(I)
      IF(DT.LT.1DO-DC.OR.DT.GT.1DO+DC) JCHECK=1
   20 CONTINUE
      IF (ITER.GT.200) GO TO 60
      IF (ITER.LT.5) ICHECK=1
      IF (ICHECK.EQ.O) RETURN 1
      IF (JCHECK.EQ.O) RETURN
      DO 50 I=1,NEQ
      DELTA(I)=ODO
   50 CONTINUE
      RETURN 2
   60 CONTINUE
      PRINT 70
      CALL PTOT
      CALL PSPEC
      CALL PPHASE
      CALL PLOOK
      STOP
C
   70 FORMAT (1H1,80('*')//' CALCULATIONS TERMINATED AT 200 ITERATIONS'/
     1/' ',80('*'))
      END
      SUBROUTINE SOLVE
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
C
C           COPY ROWS OF AR INTO MATRIX AS WHICH IS INVERTED IN SLNQ
C
C           PUT ELECTRICAL BALANCE EQUATION IN PLACE OF A MASS BALANCE
      IF (NEQ.EQ.0) RETURN
      IF (IESPEC.LT.2) GO TO 30
      TOT(IESPEC)=AR(IESPEC,IESPEC)
      DO 10 I=1,LASTT
      IF (IIN(I).EQ.0) GO TO 10
      AR(IESPEC,I)=AR(1,I)
   10 CONTINUE
      CR(IESPEC)=-ELECT
      IF (NMINS.LE.0) GO TO 30
      DO 20 I=IFM,ILM
      AR(IESPEC,I)=0D0
   20 CONTINUE
   30 CONTINUE
C           PUT ALKALINITY EQUATION IN PLACE OF MASS BALANCE
      IF (IASPEC.EQ.0) GO TO 50
      TOT(IASPEC)=AR(IASPEC,IASPEC)
      DO 40 I=1,LASTT
      AR(IASPEC,I)=AR(3,I)
   40 CONTINUE
      CR(IASPEC)=CR(3)
   50 CONTINUE
      DO 80 I=1,LASTT
      IF (IIN(I).EQ.0) GO TO 80
      K1=IIN(I)
      DO 60 J=1,LASTT
      K2=IIN(J)
      IF (K2.EQ.0) GO TO 60
      AS(K1,K2)=AR(I,J)
   60 CONTINUE
      AS(K1,NEQ1)=CR(I)
      IF (NMINS.EQ.0) GO TO 80
      DO 70 J=1,NMINS
      AS(K1,ILT+J)=AR(I,MAXT+J)
   70 CONTINUE
   80 CONTINUE
C             COPY MINERAL EQUATIONS
      IF (NMINS.EQ.0) GO TO 120
      DO 110 I=1,NMINS
      K=MAXT+I
      L=ILT+I
      DO 90 J=1,LASTT
      IF (IIN(J).LE.0) GO TO 90
      AS(L,IIN(J))=AR(K,J)
   90 CONTINUE
      DO 100 J=1,NMINS
      AS(L,ILT+J)=AR(K,MAXT+J)
  100 CONTINUE
      AS(L,NEQ1)=CR(K)
  110 CONTINUE
  120 CONTINUE
C             INVERT MATRIX.  (DX/X VALUES IN DELTA)
      CALL SLNQ
      RETURN
      END
      SUBROUTINE RESET
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      REAL*8 F
      DMIN=0.75D0
      DMAX=1.5D0
```

```
C
C          CALCULATE DELTA TOTALS IN MASSES
C
      F=1DO
      DPHPE=1DO
      IF (ITER.LT.40) GO TO 10
      DMIN=0.32DO
      DMAX=0.33DO
   10 CONTINUE
      DO 20 I=1,LASTT
      DELTOT(I)=0.ODO
   20 CONTINUE
      IF (NMINS.EQ.O) GO TO 60
      DO 40 I=IFT,ILT
      DT=0.ODO
      DO 30 J=IFM,ILM
      K=MAXT+J-ILT
      DT=DT-DELTA(J)*AR(IOUT(I),K)
   30 CONTINUE
      DELTOT(I)=DT
   40 CONTINUE
C          MAKE SURE NO NEGATIVE TOTALS RESULT
      DO 50 I=IFT,ILT
      IF (TOT(IOUT(I))+DELTOT(I).GT.0.ODO) GO TO 50
      DF=-0.9*TOT(IOUT(I))/DELTOT(I)
      F=DMIN1(F,DF)
   50 CONTINUE
   60 CONTINUE
C          ENSURE PH CHANGE REASONABLE
      IF (IIN(1).EQ.O) GO TO 70
      IF (DELTA(1).GT.-DMIN.AND.DELTA(1).LT.DMAX) GO TO 70
      DF=DABS(DMIN/DELTA(1))
      IF (DELTA(1).GT.ODO) DF=DMAX/DELTA(1)
      DPHPE=DF
   70 CONTINUE
C          ENSURE PE CHANGE REASONABLE.
      IF (IFTH.EQ.O) GO TO 80
      IF (DELTA(IFTH).GT.-DMIN.AND.DELTA(IFTH).LT.DMAX) GO TO 80
      DF=DABS(DMIN/DELTA(IFTH))
      IF (DELTA(IFTH).GT.ODO) DF=DMAX/DELTA(IFTH)
      DPHPE=DMIN1(DF,DPHPE)
   80 CONTINUE
C          SCALE DELTAS
      IF (F.EQ.1.ODO) GO TO 110
      IF (NMINS.EQ.O) GO TO 110
      DO 90 I=IFT,ILT
      DELTOT(I)=DELTOT(I)*F
   90 CONTINUE
      DO 100 I=IFM,ILM
      DELTA(I)=DELTA(I)*F
  100 CONTINUE
  110 CONTINUE
      DO 120 K=4,LASTT
      IF (K.EQ.IESPEC) GO TO 120
      IF (K.EQ.IASPEC) GO TO 120
      I=IIN(K)
      IF (I.GT.O) DELTA(I)=ODO
  120 CONTINUE
      IF (IIN(1).GT.O) DELTA(1)=DELTA(1)*DPHPE
      IF (IIN(2).GT.O) DELTA(IIN(2))=DELTA(IIN(2))*DPHPE
      IF(DPHPE.LT.1D-5.AND.DABS(DELTA(1)).LT.1D-4.AND.IIN(2).GT.0)
     1      DELTA(1)=DELTA(1)*DABS(DELTA(2)/(DELTA(1)*1D1))             N 890
      IF (IOPT(8).EQ.1) CALL PBUG(F,DPHPE)                              N 900
C           RESET ELECTRICAL BALANCE SPECIES                            N 910
      IF (IESPEC.EQ.0) GO TO 130                                        N 920
      D=DELTA(IIN(IESPEC))                                              N 930
      IF (D.LE.-1D0) D=-0.9D0                                           N 940
      IF (D.GT.66D-01) D=66D-1                                          N 950
      LA(IESPEC)=LA(IESPEC)+DLOG10(1D0+D)                               N 960
      TOT(1)=1D1**LA(1)                                                 N 970
      PH=-LA(1)                                                         N 980
  130 CONTINUE                                                          N 990
C           RESET ALKALINITY SPECIES                                    N 1000
      IF (IASPEC.EQ.0) GO TO 140                                        N 1010
      D=DELTA(IIN(IASPEC))                                              N 1020
      IF (D.LE.-1D0) D=-0.9D0                                           N 1030
      IF (D.GT.6.6D0) D=6.6D0                                           N 1040
      LA(IASPEC)=LA(IASPEC)+DLOG10(1D0+D)                               N 1050
  140 CONTINUE                                                          N 1060
C           RESET ACTIVITY OF ELECTRON                                  N 1070
      IF (IFTH.EQ.0) GO TO 150                                          N 1080
      TOT(2)=TOT(2)*(1D0+DELTA(IFTH))                                   N 1090
      LA(2)=DLOG10(TOT(2))                                              N 1100
      PE=-LA(2)                                                         N 1110
  150 CONTINUE                                                          N 1120
C           RESET TOTALS                                                N 1130
      IF (NMINS.EQ.0) GO TO 180                                         N 1140
      DO 160 I=IFT,ILT                                                  N 1150
      K=IOUT(I)                                                         N 1160
      TOT(K)=TOT(K)+DELTOT(I)                                           N 1170
      IF (TOT(K).LE.1D-30) TOT(K)=1D-30                                 N 1180
  160 CONTINUE                                                          N 1190
C           RESET TOTAL MINERALS ADDED OR REMOVED AND THE THOR.         N 1200
      DO 170 I=IFM,ILM                                                  N 1210
      K=MAXT+I-ILT                                                      N 1220
      TOT(K)=TOT(K)+DELTA(I)                                            N 1230
      IF(IOPT(3).EQ.6.AND.I.EQ.IFM) GO TO 175                           N 1240
      THOR=THOR+THMIN(I-ILT)*DELTA(I)                                   N 1250
      GO TO 170                                                         N 1260
  175 CONTINUE                                                          N 1270
      THOR=THOR+DELTA(I)*THREAC                                         N 1280
  170 CONTINUE                                                          N 1290
  180 CONTINUE                                                          N 1300
      RETURN                                                            N 1310
      END                                                               N 1320
      FUNCTION UNDER(D)                                                 N 1330
      REAL*8 D,UNDER                                                    O 10
      UNDER=0D0                                                         O 20
      IF (D.LT.-35.0D0) GO TO 10                                        O 30
      UNDER=1D5                                                         O 40
      IF (D.GT.5D0) GO TO 10                                            O 50
      UNDER=1D1**D                                                      O 60
   10 CONTINUE                                                          O 70
      RETURN                                                            O 80
      END                                                               O 90
      SUBROUTINE THORIT(T)                                              O 100
      IMPLICIT REAL*8(D),INTEGER*2(I-N)                                 P 10
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,         P 20
     1      LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL                  P 30
      DIMENSION TMIN(20)                                                P 40
                                                                        P 50
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      REAL*8 NAMELK
      REAL*4 LKLOOK,LKOLK
      COMMON /LOOK/ NAMELK(40),LKOLK(40),LKLOOK(40),DHLOOK(40),
     1       ALOOK(40,10),CLOOK(40,10),LLOOK(40,10),NLOOK(40),
     2       LOOKFL(40),NLOOKS
      T=0.0
      DALKS=0D0
      DO 10 I=1,LASTS
      IF (SFLAG(I).EQ.0) GO TO 10
      DALKS=DALKS+M(I)*ALKSP(I)
      T=T+M(I)*THSP(I)
   10 CONTINUE
      RETURN
C      *****
      ENTRY SOLN(JSOL)
C      *****
      PRINT 260, JSOL,(HEAD(JSOL,I),I=1,20)
      DO 20 I=1,MAXT
      TOT(I)=TOTAL(JSOL,I)
   20 CONTINUE
      THOR=0.0
      TC=TEMP(JSOL)
      TK=TC+273.16
      PH=-DLOG10(TOT(1))
      PE=-DLOG10(TOT(2))
      RETURN
C      *****
      ENTRY SAVE
C      *****
      IF (IOPT(7).EQ.0) RETURN
      K=IOPT(7)
      DO 30 I=1,MAXT
      TOTAL(K,I)=TOT(I)
   30 CONTINUE
      TEMP(K)=TC
      TH(K)=THOR
      DIFFZ(K)=DZOFF
      RETURN
C      *****
```

```
      ENTRY ZEROAR
C      *****
      IF (IESPEC.GE.2) IIN(1)=1
      IIN(3)=1
      DO 60 I=1,LASTT
      IF (IIN(I).EQ.0.AND.ITER.GT.1) GO TO 50
      DO 40 J=1,LASTT
      AR(I,J)=0.0D0
   40 CONTINUE
   50 CONTINUE
   60 CONTINUE
      IF (IESPEC.GE.2) IIN(1)=0
      IIN(3)=0
      RETURN
C      *****
      ENTRY CHKSPE(IERROR)
C      *****
C            CHECK MASTER SPECIES IN AQUEOUS SPECIES
      DO 80 I=1,MAXS
      IF (NSP(I).LE.0) GO TO 80
      K=NSP(I)
      DO 70 J=1,K
      L=LSP(I,J)
      IF (L.GE.1.AND.L.LE.MAXT) GO TO 70
      PRINT 270, I,SNAME(I)
      IERROR=1
   70 CONTINUE
   80 CONTINUE
C            CHECK SPECIES
      DO 100 I=MAXT1,MAXS
      K=NSP(I)
      IF (K.EQ.0) GO TO 100
      Z=0.0
      DO 90 J=1,K
      Z=Z+ZSP(LSP(I,J))*CSP(I,J)
   90 CONTINUE
      IF (ABS(ZSP(I)-Z).LT.1E-5) GO TO 100
      IERROR=1
      PRINT 280, I,SNAME(I)
  100 CONTINUE
      RETURN
C      *****
      ENTRY CHKMIN(IERROR)
C      *****
C            CHECK MINERALS FOR CHARGE AND VALENCE
      IF (NRMINS.EQ.0) GO TO 140
      THSP(2)=-1D0
      DO 130 I=1,NRMINS
      K=NMINO(I)
      Z=0.0
      THR=0.0
      DO 110 J=1,K
      Z=Z+ZSP(LMINO(I,J))*CMINO(I,J)
      THR=THR+THSP(LMINO(I,J))*CMINO(I,J)
  110 CONTINUE
      IF (ABS(Z).LT.1E-5) GO TO 120
      IERROR=2
      PRINT 290, I,MNAME(I)
  120 CONTINUE
      IF (ABS(THR-THMIN(I)).LT.1E-5) GO TO 130
      IERROR=3
      PRINT 300, I,MNAME(I)
  130 CONTINUE
      THSP(2)=0D0
  140 CONTINUE
      RETURN
C      *****
      ENTRY CHKLK
C      *****
C            CHECK LOOK MINERALS
      IF (NLOOKS.EQ.0) GO TO 170
      DO 160 I=1,NLOOKS
      K=NLOOK(I)
      Z=0.0
      DO 150 J=1,K
      Z=Z+ZSP(LLOOK(I,J))*CLOOK(I,J)
  150 CONTINUE
      IF (ABS(Z).LT.1E-5) GO TO 160
      PRINT 310, I,NAMELK(I)
  160 CONTINUE
  170 CONTINUE
      RETURN
C      *****
      ENTRY UNITS(ISOLN)
C      *****
      IASPEC=IALK(ISOLN)
      IF (IUNITS(ISOLN).EQ.0) GO TO 250
      IF (IUNITS(ISOLN).NE.1) GO TO 190
C           MMOLES/L
      DO 180 I=4,MAXT
      TOTAL(ISOLN,I)=TOTAL(ISOLN,I)*GFW(I)
  180 CONTINUE
      IUNITS(ISOLN)=2
  190 CONTINUE
      IF (IUNITS(ISOLN).NE.2) GO TO 210
C           MG/L
      DO 200 I=4,MAXT
      TOTAL(ISOLN,I)=TOTAL(ISOLN,I)/SDENS(ISOLN)
  200 CONTINUE
      IUNITS(ISOLN)=3
  210 CONTINUE
      IF (IUNITS(ISOLN).NE.3) GO TO 250
C           PPM
      TOTMG=0.0
      DO 220 I=4,MAXT
      TOTMG=TOTMG+TOTAL(ISOLN,I)
  220 CONTINUE
      C=1.0-TOTMG*1E-06
      IF (C.GT.0.0) GO TO 230
      PRINT 320
      STOP
  230 CONTINUE
      C=1.0/(C*1E+03)
      DO 240 I=4,MAXT
      IF (TOTAL(ISOLN,I).LE.0.0D0) GO TO 240
      TOTAL(ISOLN,I)=C*TOTAL(ISOLN,I)/GFW(I)
  240 CONTINUE
  250 CONTINUE
C           UNITS ARE NOW MOLALITY
      RETURN
```

```
C
  260 FORMAT (1H1,'SOLUTION NUMBER ',I1,10X,20A4/)
  270 FORMAT (1X,I4,2X,A8,5X,'SPECIES HAS A MASTER SPECIES NUMBER OUT OF
     1       RANGE')
  280 FORMAT (10X,'***** ERROR IN SPECIES NUMBER',I4,'  ',A8,'REACTION D
     1OES NOT CHARGE BALANCE.')
  290 FORMAT (10X,'***** ERROR IN MINERAL NUMBER',I4,2X,A8,' REACTION DO
     1ES NOT CHARGE BALANCE.')
  300 FORMAT (10X,'***** ERROR IN MINERAL NUMBER',I4,2X,A8,' REACTION','
     1 DOES NOT BALANCE THE SPECIFIED VALENCE.')
  310 FORMAT (10X,'***** WARNING:  LOOK MINERAL NUMBER',I4,2X,A8,' REACT
     1ION DOES NOT CHARGE BALANCE.')
  320 FORMAT (1H1,80('*')//'TERMINAL ERROR'/'TOTAL SALT PPM GREATER ','T
     1HAN 1 MILLION.'/'CHECK CONCENTRATION UNITS AND ELEMENT',' GRAM FOR
     2MULA WEIGHT INPUT',//80('*'))
      END
      SUBROUTINE PTOT
      IMPLICIT REAL*8(D),INTEGER*2(I-N)
      REAL*8 LM,M,LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,
     1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL
      COMMON /REAL8/ LM(250),M(250),LA(250),LG(250),LKSP(250),
     1       SNAME(250),TOT(50),DELTA(50),DELTOT(50),AR(50,50),
     2       AS(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),
     3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL(2,30),
     4       DALKT,DALKS,DIFFZ(2),DZOFF
      REAL*4 LKTOSP,DHSP,LKTOM,LKMINO,DHMIN,DHA
      COMMON /REAL4/ CSP(250,6),ZSP(250),THSP(250),LKTOSP(250),
     1       DHSP(250),ASP(250,5),ADHSP(250,2),TH(2),
     2       TEMP(2),HEAD(2,20),CMIN(20,10),THMIN(20),LKTOM(20),
     3       DHMIN(20),AMIN(20,5),CMCON(20,5),CMINO(20,10),
     4       LKMINO(20),VO,TITRPH(50),TITRML(50),TK,TC,XSTEP(50),
     5       TSTEP(50),CREAC(30),THREAC,TITLE(20),
     6       THMEAN(30),DHA(250),ALKSP(250),SDENS(2),GFW(30)
      INTEGER*2 GFLAG,SFLAG
      COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),
     1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,
     2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),
     3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),
     4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,
     5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,
     6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)
      REAL*8 NAMELK
      REAL*4 LKLOOK,LKOLK
      COMMON /LOOK/ NAMELK(40),LKOLK(40),LKLOOK(40),DHLOOK(40),
     1       ALOOK(40,10),CLOOK(40,10),LLOOK(40,10),NLOOK(40),
     2       LOOKFL(40),NLOOKS
      REAL*8 SUNAME(10),UNDER
      COMMON /NEUT/ SUNAME,DNEUT,NSUM(10),NSUMS,LSUM(10,50),LPOS,LNEG
      DATA IDATA /0/, DALK/'TOT ALK'/
      DATA DN1/'O2'/,DN2/'H2'/,DN3/'CHARGE'/
      DIMENSION CARD(20)
      PRINT 220
      PRINT 230
      KK=0
      DO 10 I=4,MAXT
      IF (TOT(I).EQ.0.0D0) GO TO 10
      KK=1
      DLT=DLOG10(TOT(I))
      DNAME=TNAME(I)
      IF (IASPEC.EQ.I) DNAME=DALK
      PRINT 240, DNAME,TOT(I),DLT
   10 CONTINUE
      IF (KK.EQ.0) PRINT 250
      PRINT 260
      RETURN
C      *****
      ENTRY PSPEC
C      *****
      PRINT 270
      PRINT 280, PH,PE,TOT(3),MU,TC,ELECT,THSOLN,DALKS,ITER
      IF (IASPEC.LE.0) GO TO 20
      PRINT 290, TOTAL(ISOL,IASPEC)
   20 CONTINUE
      IF (IESPEC.LE.1) GO TO 30
      D=TOT(IESPEC)-DNEUT
      PRINT 300, TNAME(IESPEC),D
   30 CONTINUE
      PRINT 310
      LM(1)=LA(1)-LG(1)
      LG(2)=0.0D0
      LM(2)=LA(2)
      LG(3)=0.0D0
      LM(3)=LA(3)
      DO 40 I=1,LASTS
      IF (SFLAG(I).EQ.0) GO TO 40
      DA=0D0
      DM=0D0
      IF (LM(I).LT.-30D0.AND.I.GT.30) GO TO 40
      IF (LM(I).GE.-60D0) DM=1D1**LM(I)
      DLA=LM(I)+LG(I)
      IF (DLA.GE.-60D0) DA=1D1**DLA
      DG=1D1**LG(I)
      PRINT 320, I,SNAME(I),ZSP(I),DM,LM(I),DA,DLA,DG,LG(I)
   40 CONTINUE
C      *****
      ENTRY PSUM
C      *****
      IF (NSUMS.EQ.0) GO TO 80
      KK=0
      DO 70 I=1,NSUMS
      LL=0
      DSUM=0D0
      K=NSUM(I)
      DO 50 J=1,K
      IF (SFLAG(LSUM(I,J)).LE.0) GO TO 50
      LL=1
      DSUM=DSUM+M(LSUM(I,J))
   50 CONTINUE
      IF (LL.EQ.0) GO TO 70
      IF (LL.EQ.0.OR.KK.NE.0) GO TO 60
      PRINT 330
      KK=1
   60 CONTINUE
      PRINT 340, SUNAME(I),DSUM
   70 CONTINUE
   80 CONTINUE
      RETURN
C      *****
      ENTRY PBUG(D,DPHPE)
C      *****
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      PRINT 350, D,CR(1),DPHPE
C           PRINT CHANGES IN PH AND PE
      IF (IIN(1).LE.0) GO TO 90
      DPH=-DLOG10(1D0+DELTA(1))
      PRINT 360, PH,DPH
   90 CONTINUE
      IF (IIN(2).LE.0) GO TO 100
      DPE=-DLOG10(1D0+DELTA(IIN(2)))
      PRINT 370, PE,DPE,CR(2)
  100 CONTINUE
C           PRINT TOTALS AND ACTIVITIES
      DO 110 K=4,LASTT
      I=IIN(K)
      IF (I.LE.0) GO TO 110
      DRT=DELTOT(I)/TOT(K)
      DA=UNDER(LA(K))
      DRA=DELTA(I)*DA
      PRINT 380, CR(K),TNAME(K),TOT(K),DELTOT(I),DRT,SNAME(K),DA,DELTA(I
     1),DRA
  110 CONTINUE
C           PRINT MINERAL TOTALS AND DELTAS
      IF (NMINS.LE.0) GO TO 130
      DO 120 I=1,NMINS
      K=MAXT+I
      J=ILT+I
      PRINT 390, CR(K),MNAME(I),TOT(K),DELTA(J)
  120 CONTINUE
  130 CONTINUE
      RETURN
C      *****
      ENTRY PPHASE
C      *****
      IF (NMINS.EQ.0) RETURN
      PRINT 400
      DO 150 I=1,NMINS
      K=NMINO(I)
      DIAP=0.0D0
      DO 140 J=1,K
      DIAP=DIAP+(LG(LMINO(I,J))+LM(LMINO(I,J)))*CMINO(I,J)
  140 CONTINUE
      DSI=DIAP-LKMINO(I)
      K=MAXT+I
      D1=TOT(K)
      IF (IOPT(3).EQ.6.AND.I.EQ.1) D1=0D0
      PRINT 410, MNAME(I),D1,DIAP,LKMINO(I),DSI
      IF (IOPT(3).EQ.6.AND.I.EQ.1) PRINT 420
  150 CONTINUE
      PRINT 430
      IF (IOPT(3).EQ.6) PRINT 440, TOT(MAXT+1),MNAME(1)
      IF (IOPT(3).NE.6) RETURN
C      *****
      ENTRY PREAC
C      *****
      PRINT 450
      DO 160 I=1,NCOMPS
      L=LREAC(I)
      IF (L.EQ.0) DN=DN3
      IF (L.LT.31) DN=TNAME(L)
      IF (L.GT.30) DN=DN1
      IF (L.GT.30.AND.THMEAN(I).LT.0) DN=DN2
      PRINT 460, CREAC(I),DN,THMEAN(I)                                  Q 1650
  160 CONTINUE                                                          Q 1660
      RETURN                                                            Q 1670
C      *****                                                             Q 1680
      ENTRY PLOOK                                                       Q 1690
C      *****                                                             Q 1700
      IF (NLOOKS.EQ.O) RETURN                                           Q 1710
      KK=O                                                              Q 1720
      DO 190 I=1,NLOOKS                                                 Q 1730
      K=NLOOK(I)                                                        Q 1740
      DIAP=ODO                                                          Q 1750
      DO 170 J=1,K                                                      Q 1760
      LL=LLOOK(I,J)                                                     Q 1770
      IF (SFLAG(LL).LE.O) GO TO 190                                     Q 1780
      DIAP=DIAP+(LG(LL)+LM(LL))*CLOOK(I,J)                              Q 1790
  170 CONTINUE                                                          Q 1800
      IF (KK.NE.O) GO TO 180                                            Q 1810
      KK=1                                                              Q 1820
      PRINT 470                                                         Q 1830
  180 CONTINUE                                                          Q 1840
      DSI=DIAP-LKLOOK(I)                                                Q 1850
      PRINT 480, NAMELK(I),DIAP,LKLOOK(I),DSI                           Q 1860
  190 CONTINUE                                                          Q 1870
      RETURN                                                            Q 1880
C      *****                                                             Q 1890
      ENTRY PDATA                                                       Q 1900
C      *****                                                             Q 1910
      IF (IOPT(1).NE.1) RETURN                                          Q 1920
      IF (IDATA.GT.O) RETURN                                            Q 1930
      IDATA=1                                                           Q 1940
      REWIND 10                                                         Q 1950
      PRINT 490                                                         Q 1960
  200 CONTINUE                                                          Q 1970
      READ (10,500,END=210) CARD                                        Q 1980
      PRINT 510, CARD                                                   Q 1990
      GO TO 200                                                         Q 2000
  210 CONTINUE                                                          Q 2010
      RETURN                                                            Q 2020
C                                                                        Q 2030
  220 FORMAT (///40X,'TOTAL MOLALITIES OF ELEMENTS'/,40X,'----- --------Q 2040
     1-- -- --------')                                                  Q 2050
  230 FORMAT (/32X,'ELEMENT',10X,'MOLALITY',9X,'LOG MOLALITY'/)         Q 2060
  240 FORMAT (32X,A8,6X,1PD13.6,8X,OPF9.4)                              Q 2070
  250 FORMAT (32X,'PURE WATER')                                         Q 2080
  260 FORMAT (//)                                                       Q 2090
  270 FORMAT (//,40X,'----DESCRIPTION OF SOLUTION----')                 Q 2100
  280 FORMAT (/,55X,'PH = ',F8.4/55X,'PE = ',F8.4/45X,'ACTIVITY H2O = ',Q 2110
     1F8.4/43X,'IONIC STRENGTH = ',F8.4/46X,'TFMPERATURE = ',F8.4/39X,'EQ 2120
     2LECTRICAL BALANCE = ',1PD12.4/53X,'THOR = ',D12.4/41X,'TOTAL ALKALQ 2130
     3INITY = ',D12.4/47X,'ITERATIONS = ',OPI3)                         Q 2140
  290 FORMAT (45X,'TOTAL CARBON = ',1PD12.4)                            Q 2150
  300 FORMAT (34X,'MOLES OF ',A8,' ADDED = ',D12.4)                     Q 2160
  310 FORMAT (///,44X,23('-')/44X,'DISTRIBUTION OF SPECIES'/44X,23('-')/Q 2170
     1/9X,'I',3X,'SPECIES',4X,'Z',6X,'MOLALITY',4X,'LOG MOLALITY',4X,'ACQ 2180
     2TIVITY',4X,'LOG ACTIVITY',5X,'GAMMA',8X,'LOG GAMMA'/)             Q 2190
  320 FORMAT (8X,I3,2X,A8,1X,F4.1,3X,3(1PD12.5,4X,OPF8.4,4X))           Q 2200
  330 FORMAT (///48X,'SUMS OF SPECIES'/)                                Q 2210
  340 FORMAT (45X,A8,' = ',1PD13.6)                                     Q 2220
  350 FORMAT (/10X,'REDUCTION FACTOR: ',1PD12.5,10X,'ELECT: ',D12.5,10X,Q 2230
     1'DPHPE: ',D12.5)                                                  Q 2240
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360 FORMAT (10X,'PH = ',F8.4,5X,'DPH = ',F8.4)                          Q 2250
370 FORMAT (10X,'PE = ',F8.4,5X,'DPE = ',F8.4,5X,'DTHOR = ',1PD12.5)  Q 2260
380 FORMAT (1X,1PD12.5,2X,A8,3(3X,D12.5),2X,A8,3(3X,D12.5))           Q 2270
390 FORMAT (1X,1PD12.5,2X,A8,3(3X,D12.5))                             Q 2280
400 FORMAT (42X,'----PHASE BOUNDARIES----'//24X,'PHASE',5X,'DELTA PHASQ 2290
   1E*',6X,'LOG IAP',6X,'LOG KT',6X,'LOG IAP/KT'/)                    Q 2300
410 FORMAT (23X,A8,2X,1PD13.6,3(4X,0PF9.4))                           Q 2310
420 FORMAT (1H+,20X,'**')                                             Q 2320
430 FORMAT (/,4X,'* NEGATIVE DELTA PHASE INDICATES PRECIPITATION ','ANQ 2330
   1D POSITIVE DELTA PHASE INDICATES DISSOLUTION.')                   Q 2340
440 FORMAT (/,3X,'** ',1PD12.6,' MOLES OF REACTION',' HAVE BEEN ADDED Q 2350
   1TO THE SOLUTION',' TO REACH THE ',A8,' PHASE BOUNDARY.')          Q 2360
450 FORMAT (/,25X,'REACTION IS:')                                     Q 2370
460 FORMAT (39X,F6.2,' MOLES OF ',A8,'  VALENCE =  ',F6.3)            Q 2380
470 FORMAT (//45X,'---- LOOK MIN IAP ----'//30X,'PHASE',8X,'LOG IAP',6Q 2390
   1X,'LOG KT',6X,'LOG IAP/KT'/)                                      Q 2400
480 FORMAT (29X,A8,3(4X,F9.4))                                        Q 2410
490 FORMAT (1H1,30X,'DATA:  CARD IMAGES FROM DISK'/)                  Q 2420
500 FORMAT (20A4)                                                     Q 2430
510 FORMAT (1X,20A4)                                                  Q 2440
    END                                                               Q 2450
    SUBROUTINE SLNQ                                                   R 10
    IMPLICIT REAL*8(A-H,O-Z),INTEGER*2(I-N)                           R 20
    REAL*8 LM,  LA,LG,LKSP,SNAME,TNAME,MNAME,TOT,AR,AS,CR,CS,         R 30
   1       LKMIN,THOR,ELECT,THSOLN,PH,PE,A,B,MU,TOTAL                 R 40
    COMMON /REAL8/ LM(250),E(250),LA(250),LG(250),LKSP(250),          R 50
   1       SNAME(250),TOT(50),    X(50),DELTOT(50),AR(50,50),         R 60
   2        A(50,50),CR(50),CS(50),TNAME(30),LKMIN(20),               R 70
   3       MNAME(20),THOR,ELECT,THSOLN,PH,PE,G,H,MU,TOTAL(2,30),      R 80
   4       DALKT,DALKS,DIFFZ(2),DZOFF                                 R 90
    INTEGER*2 GFLAG,SFLAG                                             R 100
    COMMON /INT2/ NSP(250),LSP(250,6),KFLAG(250),GFLAG(250),          R 110
   1       SFLAG(250),LASTT,LASTS,IIN(50),IOUT(50),IFE,ILE,           R 120
   2       IFTH,ILTH,IFT,ILT,IFM,ILM,NEQ,NEQ1,IESPEC,ISOLV(2),        R 130
   3       NMIN(20),LMIN(20,10),MFLAG(20),LMCON(20,5),NMCON(20),      R 140
   4       LMINO(20,10),NMINO(20),IOPT(10),NMINS,NSTEPS,NCOMPS,       R 150
   5       NELTS,NSPECS,ISTEP,LREAC(30),MAXT,MAXT1,MAXM,MAXEQ,        R 160
   6       MAXS,NRMINS,ITER,ISOL,IASPEC,IALK(2),IUNITS(2)             R 170
C                                                                      R 180
C     SOLUTION OF N LINEAR EQUATIONS IN N UNKNOWNS BY GAUSSIAN         R 190
C     ELIMINATION OR DETERMINANT EVALUTAION.                           R 200
C     A CONTAINS THE MATRIX OF THE COEFFICIENTS AND N INDICATES THE    R 210
C     ORDER OF THE MATRIX. IF J EQUALS ZERO, D CONTAINS THE VALUE OF THER 220
C     DETERMINANT. IF J DOES NOT EQUAL ZERO, X CONTAINS THE N VALUES OF R 230
C     THE UNKNOWNS.                                                    R 240
C                                                                      F 250
    J=1                                                               R 260
    N=NEQ                                                             R 270
    D=0.0                                                             R 280
    NP1=N+1                                                           R 290
    NM1=N-1                                                           R 300
    IF (IOPT(9).NE.1) GO TO 20                                        R 310
    DO 10 II=1,N                                                      R 320
    PRINT 240, (A(II,JJ),JJ=1,NP1)                                    R 330
 10 CONTINUE                                                          R 340
 20 CONTINUE                                                          R 350
    IF (N.EQ.1) GO TO 210                                             R 360
    DO 120 I=1,NM1                                                    R 370
    M=I                                                               R 380
    K=I+1                                                             R 390
```

```
      B=A(I,I)                                                          R 400
      DO 40 L=K,N                                                       R 410
      IF (DABS(B)-DABS(A(L,I))) 30,40,40                                R 420
   30 M=L                                                               R 430
      B=A(L,I)                                                          R 440
   40 CONTINUE                                                          R 450
      IF (B) 50,160,50                                                  R 460
   50 CC=A(M,I)                                                         R 470
      IF (I-M) 60,80,60                                                 R 480
   60 D=-D                                                              R 490
      DO 70 L=I,NP1                                                     R 500
      B=A(I,L)                                                          R 510
      A(I,L)=A(M,L)/CC                                                  R 520
   70 A(M,L)=B                                                          R 530
      GO TO 100                                                         R 540
   80 DO 90 L=I,NP1                                                     R 550
   90 A(I,L)=A(I,L)/CC                                                  R 560
  100 D=D*CC                                                            R 570
      DO 110 M=K,N                                                      R 580
      B=A(M,I)                                                          R 590
      DO 110 L=I,NP1                                                    R 600
      IF(DABS(B).LT.1D-25.OR.DABS(A(I,L)).LT.1D-25) GO TO 110           R 610
      A(M,L)=A(M,L)-B*A(I,L)                                            R 620
  110 CONTINUE                                                          R 630
  120 CONTINUE                                                          R 640
      D=D*A(N,N)                                                        R 650
      IF (J) 130,200,130                                                R 660
  130 X(N)=A(N,NP1)/A(N,N)                                              R 670
      K=NM1                                                             R 680
  140 M=K+1                                                             R 690
      B=0.0                                                             R 700
      DO 150 L=M,N                                                      R 710
      IF(DABS(A(K,L)).LT.1D-25.OR.DARS(X(L)).LT.1D-25) GO TO 150        R 720
      B=B+A(K,L)*X(L)                                                   R 730
  150 CONTINUE                                                          R 740
      X(K)=A(K,NP1)-B                                                   R 750
      K=K-1                                                             R 760
      IF (K) 160,200,140                                                R 770
  160 IF (J) 170,180,170                                                R 780
  170 PRINT 260                                                         R 790
      STOP                                                              R 800
  180 D=0.0                                                             R 810
      IF (IOPT(9).LT.1) GO TO 190                                       R 820
      PRINT 220                                                         R 830
      PRINT 230, (X(I),I=1,N)                                           R 840
      PRINT 250                                                         R 850
  190 CONTINUE                                                          R 860
  200 RETURN                                                            R 870
  210 CONTINUE                                                          R 880
      IF (A(1,1).EQ.0D0) GO TO 170                                      R 890
      X(1)=A(1,2)/A(1,1)                                                R 900
      GO TO 180                                                         R 910
C                                                                        R 920
C                                                                        R 930
C                                                                        R 940
  220 FORMAT (1X,'DELTA VALUES')                                        R 950
  230 FORMAT (5X,1P10D12.3)                                             R 960
  240 FORMAT (/(5X,1P10D12.3))                                          R 970
  250 FORMAT (1X)                                                       R 980
  260 FORMAT (1H1,'THE PHASE RULE HAS BEEN VIOLATED')                   R 990
```

R 1000

END

University of Alberta

Appendix 3.3 Listing of PHREEQE Thermodynamic Data Base

```
 ELEMENTS
 CA          4    40.08          CA+2
 MG          5    24.305         MG+2
 NA          6    22.9898        NA+
 K           7    39.0983        K+
 FE          8    55.847         FE+2
 MN          9    54.9380        MN+2
 AL         10    26.9815        AL+3
 BA         11   137.33          BA+2
 SR         12    87.62          SR+2
 SI         13    60.0843        SI02
 CL         14    35.453         CL-
 C          15    61.0171        HC03-
 S          16    96.06          S04-2
 N          17    62.0049        N03-
 B          18    10.81          B
 P          19    94.9714        P04-3
 F          20    18.9984        F-
 LI         21     6.941         LI+
 BR         22    79.904         BR-
 RA         23   226.0254        RA+2

SPECIES
   1
H+          100  1.0      0.0       9.0                               0.0
  0.0     0.0
    1  1.0
    2
E-          100 -1.0      0.0       0.0                               0.0
  0.0     0.0
    2  1.0
    3
H20         100  0.0      0.0       0.0                               0.0
  0.0     0.0
    3  1.0
    4
CA+2        101  2.0      0.0       6.0       5.0       0.165         0.0
  0.0     0.0
    4  1.0
    5
MG+2        101  2.0      0.0       8.0       5.5       0.20          0.0
0.0      0.0
    5  1.0
    6
NA+         101  1.0      0.0       4.0       4.0       0.075         0.0
0.0      0.0
    6  1.0
    7
K+          101  1.0      0.0       3.0       3.5       0.015         0.0
0.0      0.0
    7  1.0
    8
FE+2        100  2.0      2.0       6.0                               0.0
0.0      0.0
    8  1.0
    9
MN+2        100  2.0      2.0       6.0                               0.0
  0.0     0.0
    9  1.0
   10
```

```
AL+3        100 3.0     0.0     9.0                             0.0
 0.0       0.0
  10 1.0
  11
BA+2        100 2.0     0.0     5.0                             0.0
 0.0       0.0
  11 1.0
  12
SR+2        100 2.0     0.0     5.0                             0.0
 0.0       0.0
  12 1.0
  13
H4SIO4      100 0.0     0.0     0.0                             0.0
 0.0       0.0
  13 1.0
  14
CL-         101 -1.0   0.0      3.0     3.5     0.015           0.0
 0.0       0.0
  14 1.0
  15
CO3-2       101 -2.0    4.0     4.5     5.4     0.0             2.0
 0.0       0.0
  15 1.0
  16
SO4-2       101 -2.0    6.0     4.0     5.0     -0.04           0.0
 0.0       0.0
  16 1.0
  17
NO3-        100 -1.0    5.0     3.0                             0.0
 0.0       0.0
  17 1.0
  18
H3BO3       100 0.0     0.0     0.0                             0.0
0.0       0.0
  18 1.0
  19
PO4-3       100 -3.0    0.0     4.0                             2.0
 0.0       0.0
  19 1.0
  20
F-          100 -1.0    0.0     3.5                             0.0
 0.0       0.0
  20 1.0
  21
LI+         100 1.0     0.0     6.0                             0.0
0.0       0.0
  21 1.0
  22
BR-         100 -1.0    0.0     3.0                             0.0
0.0       0.0
  22 1.0
  23
RA+2        100 2.0     0.0     5.0                             0.0
0.0       0.0
  23 1.0
  31
OH-         200 -1.0    0.0     3.5                             1.0
-13.998   13.345
  3 1.0     1 -1.0
  32
```

```
121      O2 AQ       300 0.0      4.0      0.0                             0.0
122      -86.08     134.79
123        3 2.0      1 -4.0    2 -4.0
124       33
125      H2 AQ       200 0.0      -2.0      0.0                            0.0
126      -3.15      -1.759
127        1 2.0      2 2.0
128       34
129      HCO3-       211 -1.0     4.0      4.5       5.4        0.0       1.0
129.3     10.33      -3.604    -6.498    0.02379   2902.39
131       15 1.0      1 1.0
132       35
133      H2CO3       310 0.0      4.0      0.0                             0.0
134       16.681     -5.847    -21.3415  0.056576  6307.1
135       15 1.0      1 2.0     3 -1.0
136       36
137      CH4 AQ      400 0.0      -4.0      0.0                            0.0
138       41.071     -61.039
139       15 1.0      1 10.0    2 8.0     3 -3.0
140       40
141      HSO4-       210 -1.0     6.0      0.0                             0.0
142       1.987      4.91      -5.3505   0.0183412  557.2461
143       16 1.0      1 1.0
144       41
145      S-2         400 -2.0     -2.0      5.0                            2.0
146       20.735     -28.04
147       16 1.0      1 8.0     2 8.0     3 -4.0
148       42
149      HS-         400 -1.0     -2.0      3.5                            1.0
150       33.652     -40.14
151       16 1.0      1 9.0     2 8.0     3 -4.0
152       43
153      H2S         400 0.0      -2.0      0.0                            0.0
154       40.644     -65.44
155       16 1.0      1 10.0    2 8.0     3 -4.0
156       48
157      NO2-        400 -1.0     3.0      3.0                             0.0
158       28.57      -43.76
159       17 1.0      1 2.0     2 2.0     3 -1.0
160       49
161      N2 AQ       400 0.0      0.0      0.0                             0.0
162       207.08     -312.13
163       17 2.0      1 12.0    2 10.0    3 -6.0
164       50
165      NH3 AQ      400 0.0      -3.0      0.0                            1.0
166       109.83     -174.58
167       17 1.0      1 9.0     2 8.0     3 -3.0
168       51
169      NH4+        400 1.0      -3.0      2.5                            0.0
170       119.077    -187.055
171       17 1.0      1 10.0    2 8.0     3 -3.0
172       52
173      NH4SO4-     500 -1.0     3.0      0.0                             0.0
174       120.19    -187.055
175       17 1.0      1 10.0    2 8.0     16 1.0     3 3.0
176       57
177      H2BO3-      200 -1.0     0.0      0.0                             1.0
178      -9.240     3.224
179       18 1.0      1 -1.0
180       58
```

```
BFOH3-      200 -1.0      0.0      0.0                        0.0
-0.40      1.85
  18 1.0    20 1.0
  59
BF2OH2-     400 -1.0      0.0      0.0                        0.0
7.628      1.635
  18 1.0    20 2.0     1 1.0    3 -1.0
  60
BF3OH-      400 -1.0      0.0      0.0                        0.0
13.666     -1.58
  18 1.0     1 2.0    20 3.0    3 -2.0
  61
BF4-        400 -1.0      0.0      0.0                        0.0
20.274     -1.795
  18 1.0     1 3.0    20 4.0    3 -3.0
  65
HPO4-2      200 -2.0      0.0      4.0                        1.0
 12.346    -3.53
  19 1.0     1 1.0
  66
H2PO4-      200 -1.0      0.0      4.5                        0.0
 19.553    -4.52
  19 1.0     1 2.0
  69
HF AQ       200 0.0       0.0      0.0                        0.0
 3.169      3.46
  1 1.0     20 1.0
  70
HF2-        200 -1.0      0.0      0.0                        0.0
 3.749      4.55
  1 1.0     20 2.0
  75
CAOH+       300 1.0       0.0      0.0                        1.0
 -12.598   14.535
  4 1.0      3 1.0     1 -1.0
  76
CACO3       210 0.0       4.0      0.0                        2.0
3.153      4.023     -27.393   0.05617    4114.00
  4 1.0     15 1.0
  77
CAHCO3+     310 1.0       4.0      0.0                        1.0
11.345     1.806     -9.448    0.03709    2902.39
  4 1.0     15 1.0     1 1.0
  78
CASO4       200 0.0       6.0      0.0                        0.0
2.309      1.470
  4 1.0     16 1.0
  79
CAPO4-      200 -1.0      0.0      0.0                        2.0
6.459      3.100
  4 1.0     19 1.0
  80
CAHPO4      300 0.0       0.0      0.0                        1.0
15.085     -0.230
  4 1.0      1 1.0    19 1.0
  81
CAH2PO4+    300 1.0       0.0      0.0                        0.0
20.961     -1.120
  4 1.0      1 2.0    19 1.0
  82
```

```
CAF+        200  1.0      0.0        0.0                                  0.0
0.940      3.798
   4 1.0    20 1.0
 85
MGOH+       300  1.0      0.0        0.0                                  1.0
-11.794    15.419
   5 1.0     3 1.0     1 -1.0
 86
MGCO3       210  0.0      4.0        0.0                                  2.0
2.980      2.713     0.9910     0.00667
   5 1.0    15 1.0
 87
MGHCO3+     310  1.0      4.0        0.0                                  1.0
11.396     -2.527    -4.1790    0.01273       2902.39         2.2981E-05
   5 1.0     1 1.0    15 1.0
 88
MGSO4       200  0.0      6.0        0.0                                  0.0
2.250      1.4
   5 1.0    16 1.0
 89
MGPO4-      200 -1.0      0.0        0.0                                  2.0
6.589      3.100
   5 1.0    19 1.0
 90
MGHPO4      300  0.0      0.0        0.0                                  1.0
15.216     -0.230
   5 1.0     1 1.0    19 1.0
 91
MGH2PO4+    300  1.0      0.0        0.0                                  0.0
21.066     -1.120
   5 1.0     1 2.0    19 1.0
 92
MGF+        200  1.0      0.0        0.0                                  0.0
1.820      4.674
   5 1.0    20 1.0
 95
NACO3-      200 -1.0      4.0        0.0                                  2.0
1.268      8.911
   6 1.0    15 1.0
 96
NAHCO3      300  0.0      4.0        0.0                                  1.0
10.080     -3.604
   6 1.0     1 1.0    15 1.0
 97
NASO4-      200 -1.0      6.0        0.0                                  0.0
0.700      1.120
   6 1.0    16 1.0
 98
NAHPO4-     300 -1.0      0.0        0.0                                  1.0
12.636     -3.530
   6 1.0     1 1.0    19 1.0
100
KSO4-       200 -1.0      6.0        0.0                                  0.0
0.85       2.25
   7 1.0    16 1.0
101
KHPO4-      300 -1.0      0.0        0.0                                  1.0
12.636     -3.530
   7 1.0     1 1.0    19 1.0
105
```

```
FEOH+       300 1.0      2.0       0.0                     1.0
-9.500     13.2
  8 1.0     3 1.0    1 -1.0
106
FEOH2       300 0.0      2.0       0.0                     2.0
-20.570    28.565
  8 1.0     3 2.0    1 -2.0
107
FEOH3-      300 -1.0     2.0       0.0                     3.0
-31.000    30.300
  8 1.0     3 3.0    1 -3.0
108
FESO4       200 0.0      8.0       0.0                     0.0
2.25       3.23
  8 1.0    16 1.0
109
FE(HS)2     500 0.0     -2.0       0.0                     2.0
76.250     -120.280
  8 1.0    16 2.0    1 18.0   2 16.0   3 -8.0
110
FE(HS)3-    500 -1.0    -4.0       0.0                     3.0
111.937    -180.420
  8 1.0    16 3.0    1 27.0   2 24.0   3 -12.0
111
FEHPO4      300 0.0      2.0       0.0                     1.0
15.946     -3.530
  8 1.0     1 1.0   19 1.0
112
FEH2PO4+    300 1.0      2.0       0.0                     0.0
22.253     -4.520
  8 1.0     1 2.0   19 1.0
115
FE+3        200 3.0      3.0       9.0                     0.0
-13.032    10.0
  8 1.0     2 -1.0
116
FEOH+2      400 2.0      3.0       0.0                     0.0
-15.22     20.4
  8 1.0     3 1.0    2 -1.0   1 -1.0
117
FEOH2+      400 1.0      3.0       0.0                     0.0
-18.70     10.0
  8 1.0     3 2.0    1 -2.0   2 -1.0
118
FEOH3       400 0.0      3.0       0.0                     1.0
-26.63     10.0
  8 1.0     3 3.0    1 -3.0   2 -1.0
119
FEOH4-      400 -1.0     3.0       0.0                     2.0
-34.63     10.0
  8 1.0     3 4.0    1 -4.0   2 -1.0
120
FE2OH2+4    400 4.0      6.0       0.0                     0.0
-29.01     33.5
  8 2.0     3 2.0    1 -2.0   2 -2.0
121
FE3OH4+5    400 5.0      9.0       0.0                     0.0
-45.4      44.3
  8 3.0     3 4.0    1 -4.0   2 -3.0
122
```

```
FECL+2      300 2.0      3.0       0.0                    0.0
-11.55     15.6
  8 1.0     14 1.0     2 -1.0
123
FECL2+      300 1.0      3.0       0.0                    0.0
-10.90     10.0
  8 1.0     14 2.0     2 -1.0
124
FECL3       300 0.0      3.0       0.0                    0.0
-11.90     10.0
  8 1.0     14 3.0     2 -1.0
125
FESO4+      300 1.0      9.0       0.0                    0.0
-9.11      13.91
  8 1.0     16 1.0     2 -1.0
126
FESO42-     300 -1.0     15.0      0.0                    0.0
-7.61      14.60
  8 1.0     16 2.0     2 -1.0
127
FEHPO4+     400 1.0      3.0       0.0                    1.0
 4.74      12.23
  8 1.0      1 1.0    19 1.0     2 -1.0
128
FEH2P+2     400 2.0      3.0       0.0                    0.0
 11.95     5.48
  8 1.0      1 2.0    19 1.0     2 -1.0
129
FEF+2       300 2.0      3.0       0.0                    0.0
-6.8       12.7
  8 1.0     20 1.0     2 -1.0
130
FEF2+       300 1.0      3.0       0.0                    0.0
-2.2       14.7
  8 1.0     20 2.0     2 -1.0
131
FEF3        300 0.0      3.0       0.0                    0.0
0.97       15.4
  8 1.0     20 3.0     2 -1.0
135
MNOH+       300 1.0      2.0       0.0                    1.0
-10.59     14.40
  9 1.0      3 1.0     1 -1.0
136
MNOH3-      300 -1.0     2.0       0.0                    3.0
-34.80     0.0
  9 1.0      3 3.0     1 -3.0
137
MNCL+       200 1.0      2.0       0.0                    0.0
 0.607     0.0
  9 1.0     14 1.0
138
MNCL2       200 0.0      2.0       0.0                    0.0
 0.041     0.0
  9 1.0     14 2.0
139
MNCL3-      200 -1.0     2.0       0.0                    0.0
 -0.305    0.0
  9 1.0     14 3.0
140
```

```
MNHCO3+      300  1.0      2.0       0.0                      1.0
  11.60     -3.604
   9  1.0    15  1.0     1  1.0
141
MNSO4        200  0.0      8.0       0.0                      0.0
  2.26      2.17
   9  1.0    16  1.0
142
MN(NO3)2     200  0.0     12.0       0.0                      0.0
0.6         -0.396
   9  1.0    17  2.0
143
MNF+         200  1.0      2.0       0.0                      0.0
  0.85      0.0
   9  1.0    20  1.0
144
MN+3         200  3.0      3.0       0.0                      0.0
  -25.507    25.76
   9  1.0     2 -1.0
145
MNO4-2       400 -2.0      6.0       0.0                      0.0
  -118.440  150.02
   9  1.0     3  4.0     1 -8.0    2 -4.0
146
MNO4-        400 -1.0      7.0       3.5                      0.0
  -127.824  176.62
   9  1.0     3  4.0     1 -8.0    2 -5.0
150
ALOH+2       300  2.0      0.0       0.0                      0.0
 -4.99      11.9
  10  1.0     3  1.0     1 -1.0
151
ALOH2+       300  1.0      0.0       0.0                      0.0
 -10.1      0.0
  10  1.0     3  2.0     1 -2.0
152
ALOH3        300  0.0      0.0       0.0                      1.0
 -16.0      0.0
  10  1.0     3  3.0     1 -3.0
153
ALOH4-       300 -1.0      0.0       0.0                      2.0
 -23.000    44.06
  10  1.0     3  4.0     1 -4.0
154
ALSO4+       200  1.0      6.0       0.0                      0.0
  3.02       2.15
  10  1.0    16  1.0
155
ALSO42-      200 -1.0     12.0       0.0                      0.0
  4.92       2.84
  10  1.0    16  2.0
156
ALF+2        200  2.0      0.0       0.0                      0.0
  7.01      0.0
  10  1.0    20  1.0
157
ALF2+        200  1.0      0.0       0.0                      0.0
  12.75     20.0
  10  1.0    20  2.0
158
```

```
481     ALF3       200 0.0      0.0      0.0                        0.0
482      17.02    2.50
483      10 1.0   20 3.0
484     159
485     ALF4-      200 -1.0     0.0      0.0                        0.0
486      19.72    0.0
487      10 1.0   20 4.0
488     163
489     BAOH+      300 1.0      0.0      0.0                        1.0
490      -13.358  15.095
491      11 1.0    3 1.0    1 -1.0
492     165
493     SROH+      300 1.0      0.0      0.0                        1.0
494      -13.178  14.495
495      12 1.0    3 1.0    1 -1.0
496     170
497     H3SIO4-    210 -1.0     0.0      0.0                        1.0
498      -9.929   8.936    6.368      -0.016346   -3405.9
499      13 1.0    1 -1.0
500     171
501     H2SIO4-2   210 -2.0     0.0      0.0                        2.0
502      -21.617  29.717   39.478     -0.065927   -12355.1
503      13 1.0    1 -2.0
504     172
505     SIF6-2     400 -2.0     0.0      0.0                        0.0
506      30.18    -16.26
507      13 1.0    1 4.0    20 6.0    3 -4.0
508     181
509     LISO4-     200 -1.0     6.0      0.0                        0.0
510     0.640     0.0
511      21 1.0   16 1.0
512     200
513     BASO4      200 0.0      6.0      0.0                        0.0
514     0.01      0.0
515      11 1.0   16 1.0
516     201
517     RASO4      200 0.0      6.0      0.0                        0.0
518     -0.01     -0.02
519      23 1.0   16 1.0
520
521     LOOK MIN
522     CALCITE    2   4.0        -8.47      -2.58        1
523      15 1.0          4 1.0
524     13.543     -0.0401      -3000.0
525     DOLOMITE   3   8.0        -17.020    -8.29        0
526      4 1.0           5 1.0          15 2.0
527     SIDERITE   2   6.0        -10.55     -5.328       0
528      8 1.0           15 1.0
529     RHODOCHR   2   6.0        -10.41     -2.079       0
530      9 1.0           15 1.0
531     STRONTIT   2           4.0      -9.25      -0.69  0
532      12        1.0  15          1.0
533     GYPSUM     3   6.0        -4.602     -0.028       0
534      4 1.0           16 1.0         3 2.0
535     CELESTIT   2   6.0        -6.465     -0.47        0
536      12 1.0          16 1.0
537     BARITE     2   6.0        -9.976     6.28         0
538      11 1.0          16 1.0
539     HYDROXAP   4   0.0        -3.421     -36.155      0
540      3 1.0           65 3.0         4 5.0        1 -4.0
```

```
541     FLUORITE    2   0.0       -10.96     4.71            0
542       4 1.0         20 2.0
543     CHALCEDY    2   0.0       -3.523     4.615           0
544       13 1.0         3 -2.0
545     QUARTZ      2   0.0       -4.006     6.22            0
546       13 1.0         3 -2.0
547     GIBBSITE    3          0.0      8.77      -22.8      0
548       10         1.0   3        3.0   1        -3.0
549     KAOLINIT    4          0.0   -36.921    49.150       0
550       3        -7.0   1         2.0  13          2.0 153          2.0
551     SEPIOLIT    4   0.0       -40.079   26.532           0
552       5 2.0         13 3.0          31 4.0         3 -4.5
553     HEMATITE    3   6.0       -4.008     -30.845         0
554       115 2.0        3 3.0           1 -6.0
555     GOETHITE    3   3.0       0.5        -14.48          0
556       115 1.0        3 2.0           1 -3.0
557     FEOH3A      3   3.0       4.891      0.0             0
558       115 1.0        3 3.0           1 -3.0
559     PYRITE      4        0.0   -18.48      11.3          0
560       1  -2.0        2  -2.0         8  1.0        42  2.0
561     FES PPT     3   0.0       -3.915     0.0             0
562       8 1.0         42 1.0           1 -1.0
563     VIVIANIT    3   6.0       -36.000    0.0             0
564       8 3.0         19 2.0           3 8.0
565     PCO2        2       4.0     -1.466     -4.708        0
566       35  1.0        3 -1.0
567     O2 GAS      1     4.0       -2.96       -1.844       0
568       32  1.0
569     H2 GAS      1      -2.0     -3.15       -1.759       0
570       33  1.0
571     MIRABILI    3   6.0       -1.1130    -18.987         0      0.0
572       6 2.0         16 1.0           3 10.0
573     PORTLAND    3    0.0      -5.29      -4.01           0
574       4 1.0         31 2.0
575     SILGEL      2   0.0       -3.017     4.44            0
576       13 1.0         3 -2.0
577     MONTMOR     7         0.99    -29.78      0.0        0
578       13        3.82   4        0.45   3        -9.16   1       -0.84   6       0 42
579      115        0.33 153        1.47
580     ANHYDRIT    2   6.0       -4.12      -4.30           0
581       4 1.0         16 1.0
582     RASO4(S)    2   6.0      -10.42      8.18            0
583       23 1.0        16 1.0
584
585     END
End of file
```

Appendix 3.4 Listing of PHRQIN Program

```
      PROGRAM PHRQIN
C
C
C              **PROGRAM TO FORMAT INPUT DATA FOR PHREEQE**
C
C        THIS INTERACTIVE PROGRAM WILL SET UP THE INPUT FILE OF PHREEQE
C        BY ASKING THE USER VALUES OF THE VARIABLES.  ALL QUESTIONS
C        SHOULD BE SELF-EXPLANATORY.  IF YOU DON'T UNDERSTAND THE
C        USE OF A CERTAIN VARIABLE, A SHORT EXPLANATION OF THAT
C        VARIABLE IS AVAILABLE BY ENTERING A "?".  IN SOME CASES,
C        HELP IS ALSO OBTAINABLE BY ENTERING SOMETHING THAT IS
C        INCOMPATIBLE WITH THE VARIABLE OR JUST A <CR>.  TO BE
C        ON THE SAFE SIDE, HOWEVER, A "?" IS RECOMMENDED.
C
C        AFTER EACH RECORD OF CARD IS COMPLETED, IT WILL BE PRINTED
C        ON THE SCREEN AND YOU WILL BE ASKED WHETHER THIS CARD
C        IS ALL RIGHT.  IF YOU ANSWER 'NO', THE PROGRAM WILL TAKE
C        THE VARIABLES ON THE CARD, PRINT THEM INDIVIDUALLY, AND YOU
C        WILL BE GIVEN THE CHANCE OF CORRECTING ANY OF THEM.  IF YOU
C        ANSWER 'YES', THE PROGRAM WILL GO ON TO THE NEXT CARD AND YOU
C        WILL NOT HAVE ANY MORE CHANCE OF CORRECTING ANY VARIABLES ON
C        THAT CARD.
C
C
C           -WRITTEN BY GEORGE W. FLEMING  AND  L. NIEL PLUMMER-
C                                  SUMMER, 1980
C                         LAST UPDATE--AUGUST, 1983
C
C         MTS-COMPATABLE VERSION BY J.T. FREEMAN  JULY, 1984
C
C    ****************************************************************
C    USER'S MANUAL AVAILABLE BY RUNNING *TEXTFORM ON FWSS:PHRQ.INUSER
C    ****************************************************************
C
C
      DIMENSION IOPT(9),LT(2,30),DTOT(2,30),ADHSP(250,2),ASP(250,5)
     1,LSP(250,6),CSP(250,6),AMIN(2,100,5),XTEMP(50),XSTEP(50)
     2,LREAC(30),CREAC(30),THMEAN(30),JSUB(11)
     3,NELT(30),TGFW(30),NI(250),NSP(250),KFLAG(250),ZSP(250),ISDEL(250)
     4,THSP(250),ALKSP(250),NMINO(2,100),THMIN(2,100),MFLAG(2,100)
     5,LMIN(2,100,10),CMIN(2,100,10),IMIN(2),NSUM(10),LSUM(10,50)
     6,IMORE(11),TEMP(2),PE(2),PH(2),SDENS(2),IUNITS(2),HEAD(2)
     7,NTOTS(2),IREQ(11),ICHECK(2,4:30),MUSED(100)
     8,IORDER(11),NSOLUT(2),IALK(2),SIMIN(2,100),IMAX(9)
      COMMON /NEW1/ LINE
      COMMON /NEW2/ JLINE
      COMMON /NEW3/ ICOL1,ICOL4
      COMMON /NEW4/ CHARP,FP
      COMMON /REFF/ JOPT,IOPEN
      COMMON /REFF1/ I
      COMMON /PN/ NFLAG
      COMMON /EE/ EXIT,LIST,JFLAG
      COMMON /PT1/ MNAMEO,THMINO,LKTOMO,DHMINO
     1,SIMINO,CMINO,AMINO,SPEC
      COMMON /PT2/ NMINOO(100),MFLAGO(100),LMINO(100,10)
     1,ICOL2(0:30),OPV(30),ICOL3,IMINO
      REAL ICOL3(0:30)
      LOGICAL YN,EXIT,LIST,STOP,OK
      INTEGER GFLAG(250),OUT
      CHARACTER *16 CHARP
      CHARACTER *80 TITLE,LINE,HEAD,JLINE(3)
      CHARACTER *72 TFILE
      CHARACTER *4 FP
      CHARACTER *8 SUB(11),KYWORD(20),TNAME(30),SNAME(250),MNAME(2,100)
     1,SUNAME(10),DELETE,ICOL1(0:30),ICOL4(0:30),CSP,MNAMEO(100)
     2,SPEC(30),CREAC,THMEAN,EQUIWT,SUBO(11)
      CHARACTER *12 OPTION,VO,PH,PE,TEMP,SDENS,TGFW,ZSP,THSP,DHA(250)
     1,ADHSP,ALKSP,LKTOSP(250),THMIN,LKTOM(2,100),DHMIN(2,100),SIMIN
     2,XTEMP,XSTEP,DTOT,CMIN,DHSP(250),AMIN,ASP,BLANK,CMINO(100,10)
     3,THMINO(100),LKTOMO(100),DHMINO(100),SIMINO(100),AMINO(100,5)
      DATA SUB/'SOLUTION','ELEMENTS','SPECIES ','MINERALS','LOOK MIN',
     1'TEMP    ','STEPS   ','REACTION','NEUTRAL ','SUMS    ','END     '/
     2SUBO/'solution','elements','species ','minerals','look min',
     3'temp    ','steps   ','reaction','neutral ','sums    ','end     '/
      DATA OPTION/'OPTION CARD'/BLANK/'     0.0     '/
      DATA IMAX/ 1,2,6,3,1,1,2,1,1/IORDER/2,3,1,4,5,6,7,8,9,10,11/
     1IMORE/1,1,1,1,1,0,0,0,0,1,0/DELETE/'DELETE  '/
C
C        READ NECESSARY DATA IN RDFILE FROM UNITS 11(PHRQ.MINDAT)
C        AND 12(PHRQ.DATBASE).
C
      CALL RDFILE(SUB)
      CLOSE (UNIT=11)
      CLOSE (UNIT=12)
      WRITE (1,1)
    1 FORMAT ('ENTER OUTPUT FILE NAME')
      READ (1,20) TFILE
   20 FORMAT (A72)
      OPEN (UNIT=10,FILE=TFILE,STATUS='UNKNOWN')
C
      ITIME=0
C
C     CALL SUBROUTINE OPEN WHICH ASKS USER WHETHER OR NOT HE
C     WISHES TO USE A REFERENCE FILE FOR DATA ACQUISITION
C
    2 CALL OPEN (ITIME)
    3 JOPEN=IOPEN
C
C     INITIALIZE VARIABLES
C
      DO 101 K=1,11
      IREQ(K)=0
  101 JSUB(K)=0
      DO 103 K=1,100
  103 MUSED(K)=0
      DO 104 K=1,250
  104 ISDEL(K)=0
      DO 105 K=4,30
      DO 105 K2=1,2
  105 ICHECK(K2,K)=0
      DO 106 K=1,50
      XSTEP(K)=BLANK
  106 XTEMP(K)=BLANK
      DO 102 K=1,30
      LREAC(K)=0
      CREAC(K)=BLANK
  102 THMEAN(K)=BLANK
      DO 108 K=1,9
        IMAX(K)=0
  108 CONTINUE
```

```
      KDUM=1
      ISUB=0
      IELEM=0
      IMIN(1)=0
      IDELET=0
      JDELET=0
      IMIN(2)=0
      ISPECI=0
      ISUM=0
      NSTART=1
      OUT=10
      I=0
      ISOL=0
      IERROR=0
      JOPT=0
      JUMP=0
C
      IF (IOPEN.EQ.0)GO TO 10
C
C         EXPLANATION OF SOME FLAGS:
C
C         ICHECK     -->MAKE SURE THAT FOR EVERY MASTER SPECIES
C                       ENTERED, THERE IS A CORRESPONDING ELEMENT
C         IERROR     -->FLAG TO SEE IF IT IS OK TO END THE
C                       SIMULATION.
C         JSUB       -->KEEPS TRACK OF WHICH DATA BLOCK IS USED,
C                       AND WHICH ISN'T.
C         MUSED      -->KEEPS TRACK OF WHICH MINERAL DATA HAS BEEN
C                       CALLED.
C         ISDEL      -->SPECIES TO BE DELETED
C         IELEM      -->NUMBER OF ELEMENTS.
C         IMIN(1)    -->NUMBER OF MINERALS.
C         IMIN(2)    -->NUMBER OF LOOK MINS
C         IMINO      -->NUMBER OF PRE-CONSTRUCTED MINERAL DATA
C         ISPECI     -->NUMBER OF SPECIES
C         ISUM       -->NUMBER OF SUMS.
C         IDELET     -->SET TO 1 IF ALL MINERALS ARE TO BE DELETED.
C         JDELET     -->SET TO 1 IF ALL OLD SUMS ARE TO BE DELETED
C         I          -->WHICH DATA BLOCK IS THE USER USING
C         NFLAG      -->SET TO 1 IF THE VARIABLE IS SEEN BY THE USER
C                       THE SECOND TIME.
C         JFLAG      -->USER'S RESPONSE FLAG
C         IREQ       -->WHICH DATA BLOCKS ARE REQUIRED
C         IMAST      -->IS THE SPECIES OR ELEMENT ENTERED 'MASTER'?
C         IOPEN      -->IF IT IS > 0, A REFERENCE FILE IS USED.
C         JOPT       -->IF IOPEN > 0, WHAT DOES THE USER WANT TO DO
C                       WITH EACH CARD.
C         ITIME      -->NUMBER OF TIMES SUBROUTINE OPEN IS CALLED
C         ILINE      -->NUMBER OF LINES TO BE READ FROM THE REFERENCE
C                       FILE.
C         IMAX       -->MAXIMUM VALUES PERMITTED FOR EACH OPTION.
C         IORDER     -->THE ORDER THAT THE DATA BLOCKS ARE TO BE
C                       PRINTED.
C         IMORE      -->IS IT OK TO CALL A CERTAIN DATA BLOCK MORE
C                       THAN ONCE.
C
C
C -----------------------
C TITLE CARD DATA BLOCK
C -----------------------
```

```
C
      WRITE (1,94)
   94 FORMAT (/'TITLE CARD:')
      CALL REF (1,1,4)
      IF (IOPEN.EQ.0.OR.JOPT.NE.1)GO TO 10
      TITLE=JLINE(1)
      GO TO 90
   10 NFLAG=0
      CHARP='THE TITLE'
      FP='A80 '
      CALL QUESTA (0,9,TITLE,0,0,*1000)
      WRITE (1,9110)
      WRITE (1,1731) TITLE
      IF (.NOT.OK(KDUM)) GO TO 10
C
C  ----------------------
C  OPTION CARD DATA BLOCK
C  ----------------------
C
   90 IF (IOPEN.EQ.0)GO TO 91
      WRITE (1,95) OPTION
   95 FORMAT (/,A11,':')
      CALL REF (1,1,1)
      IF (JOPT.EQ.3.OR.IOPEN.EQ.0)GO TO 91
      READ (JLINE(1),9991)(IOPT(N),N=1,9),NSTEPS,NCOMPS,VO
      IF (JOPT.EQ.1)GO TO 92
      GO TO 91
C
C        *** IOPTS ***
C
   91 CHARP='IOPT'
      FP='I1  '
      DO 200 N=NSTART,9
      CALL QUESTB (N,4,IOPT(N),0,IMAX(N),0,*290)
  200 CONTINUE
      IF ((IOPT(3).LE.4.AND.IOPT(3).GE.1).OR.IOPT(4).GE.2) GO TO 250
      NSTEPS=0
      GO TO 300
C
C        *** NSTEPS ***
C
  250 CHARP='NSTEPS'
      FP='I2  '
      CALL QUESTB (0,6,NSTEPS,1,50,0,*2200)
  300 IF (IOPT(3).EQ.3.OR.IOPT(3).EQ.4.OR.IOPT(3).EQ.6)GO TO 301
      NCOMPS=0
      GO TO 400
C
C        *** NCOMPS ***
C
  301 CHARP='NCOMPS'
      FP='I2  '
      CALL QUESTB (0,6,NCOMPS,1,100,0,*2300)
  400 IF (IOPT(3).EQ.2) GO TO 430
      VO=' 0.0'
      GO TO 500
C
C        *** VO ***
C
  430 CHARP='VO'
```

```
      FP='A10 '
      CALL QUESTA (0,2,VO,1,0,*2400)
  500 WRITE (1,9110)
      WRITE (1,9991) (IOPT(I),I=1,9),NSTEPS,NCOMPS,VO
      IF (OK(KDUM)) GO TO 92
      NSTART=1
      GO TO 91
C
C          SET FLAGS FOR THE KEYWORD DATA BLOCKS THAT ARE REQUIRED
C          THIS WAY THE USER CANNOT FORGET ANY NECESSARY DATA.
C
   92 IF (IOPT(3).EQ.5.OR.IOPT(3).EQ.6)IREQ(4)=1
      IF (IOPT(2).EQ.2)IREQ(9)=1
      IF (IOPT(3).GE.1.AND.IOPT(3).LE.4)IREQ(7)=1
      IF (IOPT(3).EQ.3.OR.IOPT(3).EQ.4.OR.IOPT(3).EQ.6)IREQ(8)=1
      IF (IOPT(4).NE.0)IREQ(6)=1
C
C          KEYWORD DATA BLOCKS.
C          THE PROGRAM IS DESIGNED SO THAT THE DATA BLOCKS CAN BE
C          ENTERED IN ANY ORDER.  CERTAIN DATA BLOCKS, SUCH AS
C          'ELEMENTS', 'SPECIES', 'MINERALS', ETC., CAN BE CALLED
C          UPON MORE THAN ONCE.  IN THAT CASE, NEW ELEMENTS, SPECIES,
C          MINERALS, ETC., WILL JUST BE ATTACHED TO THE END OF THE
C          DATA BLOCK.  AT THE END OF THE SIMULATION, THE PROGRAM
C          RE-ARRANGES THE DATA BLOCKS AND PRINTS THEM IN A PREFERRED
C          ORDER.
C
C          IF YOU ACCIDENTALLY ENTERED A DATA BLOCK THAT YOU DO NOT
C          WISH TO USE, ENTER 'EXIT' AS THE FIRST COMMAND AFTER YOU'VE
C          ENTERED THE DATA BLOCK NAME.
C
  531 ISUB=1
  621 WRITE(1,601)
  601 FORMAT (/,19('*'),/,'KEYWORD DATA BLOCKS',/,19('*'),//)
      IF (IOPEN.EQ.0)GO TO 604
  612 READ (13,9001,END=608,ERR=650) KYWORD(ISUB),NSOL
      DO 609 I=1,11
  609 IF (KYWORD(ISUB).EQ.SUB(I))GO TO 615
  650 GO TO 612
C
C          IF THE KEYWORD DATA BLOCKS ARE NOT ALLOWED, DON'T BOTHER
C          TO ASK THE USER.
C
  615 IF (I.EQ.6.AND.IOPT(4).EQ.0)GO TO 612
      IF (I.EQ.7.AND.(IOPT(3).EQ.0.OR.IOPT(3).EQ.5.OR.IOPT(3).EQ.6))
     1GO TO 612
      IF (I.EQ.8.AND.NCOMPS.EQ.0)GO TO 612
      IF (I.EQ.9.AND.IOPT(2).NE.2)GO TO 612
      WRITE (1,613)
  613 FORMAT (/,'KEYWORD:')
      IF (I.EQ.1)GO TO 660
      WRITE (1,9050)KYWORD(ISUB)
      GO TO 670
  660 WRITE (1,9001)KYWORD(ISUB),NSOL
  670 CALL REF (0,1,2)
      IF (I.NE.11)GO TO 120
      IOPEN=0
  120 IF (JOPT.EQ.1)GO TO 620
      JOPT=0
      IF (I.EQ.11) GO TO 604
      GO TO 621
  608 IOPEN=0
      GO TO 531
  604 WRITE (1,603)
  603 FORMAT (/,'ENTER KEYWORD.')
      READ (1,20) LINE
C
C         CHECK TO SEE IF HELP WITH KEYWORDS IS REQUESTED
C
      READ (LINE,*,ERR=622) IHELP
C     GO TO 622
      IF (IHELP.GT.11.OR.IHELP.LT.1)GO TO 4200
C
C         HE ASKED FOR HELP..
C
      GO TO (4148,4150,4146,4152,4154,4156,4158,4160,4162,4164,4166),
     1IHELP
  622 READ (LINE,9050,ERR=4200) KYWORD(ISUB)
      READ (LINE,810,ERR=820) NSOL
  810 FORMAT (9X,I1)
      GO TO 830
  820 NSOL=0
C
C         DETERMINE IF LEGITIMATE KEYWORD WAS ENTERED
C
  830 DO 610 I=1,11
      IF (KYWORD(ISUB).EQ.SUBO(I)) GO TO 620
      IF (KYWORD(ISUB).EQ.SUB(I)) GO TO 620
  610 CONTINUE
      GO TO 4200
C
C         AH, A LEGITIMATE KEYWORD...
C
  620 IF(JSUB(I).EQ.1.AND.IMORE(I).EQ.0)GO TO 630
      JSUB(I)=1
      GO TO 640
  630 WRITE (1,635)
  635 FORMAT (/,'YOU HAVE ALREADY USED IT ONCE'/)
      GO TO 621
  640 WRITE (1,639) KYWORD(ISUB)
  639 FORMAT (//,8('-'),/,A8,/,8('-'),//)
      II=I-3
C
C         GO TO ADDRESS OF APPROPRIATE KEYWORD DATA BLOCK
C
      GO TO (1700,1725,1750,3260,3250,3270,3280,3900,6000,7000,950), I
      STOP
C
C  -------------------
C  SOLUTION DATA BLOCK
C  -------------------
C
 1700 CONTINUE
      ISOL=ISOL+1
      IF (ISOL.LE.2) GO TO 1510
      WRITE (1,1300)
 1300 FORMAT ('ONLY 2 SOLUTIONS ARE ALLOWED. ')
      ISOL=2
      GO TO 531
 1510 IF (IOPEN.EQ.0.AND.NSOL.EQ.0)GO TO 1739
```

```
      IF (NSOL.EQ.1.OR.NSOL.EQ.2) GO TO 1500
      JOPT=0
      GO TO 1492
 1500 NSOLUT(ISOL)=NSOL
      IF (IOPEN.EQ.0) GO TO 1400
      WRITE (1,1736) SUB(I)
 1736 FORMAT (/,A8,' CARD:')
      CALL REF (2,1,0)
      READ (JLINE(1),1731) HEAD(ISOL)
 1731 FORMAT (A80)
      READ (JLINE(2),9003) NTOTS(ISOL),IALK(ISOL),IUNITS(ISOL),PH
     1 (ISOL),PE(ISOL),TEMP(ISOL),SDENS(ISOL)
      IF (NTOTS(ISOL).EQ.0)GO TO 1734
      CALL REF (1,1,0)
      READ (JLINE(1),9004) (LT(ISOL,M),DTOT(ISOL,M),M=1,5)
      IF (NTOTS(ISOL).LE.5)GO TO 1734
      LLINE=INT((NTOTS(ISOL)-1)/5)
      DO 1738 KLINE=1,LLINE
      CALL REF (1,1,0)
 1738 READ (JLINE(1),9004) (LT(ISOL,M),DTOT(ISOL,M),M=KLINE*5+1,
     1 (KLINE+1)*5)
 1734 CALL REF (0,1,1)
      IF (JOPT.EQ.1.AND.IALK(ISOL).GT.0)GO TO 1752
      IF (JOPT.EQ.1)GO TO 531
C
C        *** SOLUTION NUMBER ***
C
 1739 CHARP='SOLUTION NUMBER'
      FP='I1  '
      CALL QUESTB (0,15,NSOLUT(ISOL),1,2,1,*1492)
      IF (.NOT.EXIT)GO TO 1730
      JSUB(1)=0
 1753 GO TO 531
 1730 WRITE (1,1001) NSOLUT(ISOL)
 1001 FORMAT (/,'SOLUTION',1X,I1)
      IF (.NOT.OK(KDUM)) GO TO 1739
 1400 IREQ(1)=0
C
C        *** HEAD ***
C
      IF (JOPT.EQ.2) NFLAG=1
 1488 CHARP='HEAD'
      FP='A80 '
      CALL QUESTA (0,4,HEAD(ISOL),0,0,*4300)
      WRITE (1,9110)
      WRITE (1,1731)HEAD(ISOL)
      IF (.NOT.OK(KDUM)) GO TO 1488
C
C        *** NTOTS ***
C
 1713 CHARP='NTOTS'
      FP='I2  '
      CALL QUESTB (0,5,NTOTS(ISOL),0,100,0,*4320)
 1714 IF (NTOTS(ISOL).NE.0)GO TO 1727
      IALK(ISOL)=0
      IUNITS(ISOL)=0
      GO TO 1718
C
C        *** IALK ***
C
```

```
 1727 CHARP='IALK'
      FP='I3  '
      CALL QUESTB (0,4,IALK(ISOL),0,0,0,*4340)
      JUMP=0
      IF (IALK(ISOL)) 4340,1715,1708
 1708 IF (IALK(ISOL).GT.30.OR.IALK(ISOL).LT.4) GO TO 4340
C
C       *** IUNITS ***
C
 1715 CHARP='IUNITS'
      FP='I2  '
      CALL QUESTB (0,6,IUNITS(ISOL),0,3,0,*4360)
C
C       *** PH ***
C
 1718 CHARP='PH'
      FP='A10 '
      CALL QUESTA (0,2,PH(ISOL),1,0,*4380)
C
C       *** PE ***
C
 1723 CHARP='PE'
      FP='A10 '
      CALL QUESTA (0,2,PE(ISOL),1,0,*4400)
C
C       *** TEMP ***
C
 1724 CHARP='TEMP'
      FP='A10 '
      CALL QUESTA (0,4,TEMP(ISOL),1,0,*4420)
      IF (IUNITS(ISOL).NE.0) GO TO 1482
      SDENS(ISOL)=' 1.0'
      GO TO 1490
C
C       *** SDENS ***
C
 1482 CHARP='SDENS'
      FP='A10 '
      CALL QUESTA (0,5,SDENS(ISOL),1,0,*4440)
 1490 WRITE (1,9110)
      WRITE (1,9003) NTOTS(ISOL),IALK(ISOL),IUNITS(ISOL),PH(ISOL)
     1,PE(ISOL),TEMP(ISOL),SDENS(ISOL)
      IF (.NOT.OK(KDUM)) GO TO 1713
      IF (IALK(ISOL).EQ.0)GO TO 1726
 1752 WRITE (1,1006)
 1006 FORMAT (/,'HAS THE APPROPRIATE CARBON ELEMENT-CARD BEEN',
     1' CONSTRUCTED?')
      JUMP=1
      IF (.NOT.YN(KDUM)) GO TO 1728
      GO TO (1726,1753,1726,1726),JOPT+1
C
C          ADD AN EXTRA ELEMENT CARD FOR HIM..
C
 1728 WRITE (1,1709)
 1709 FORMAT (/,'WHAT IS THE GRAM EQUIVALENT WEIGHT (GRAMS/EQUIVALENT'
     1,') OF THE',/,'CHEMICAL SPECIES IN WHICH THE ALKALINITY IS',
     2' REPORTED?')
      WRITE (1,1710)
 1710 FORMAT (//,'FOR EXAMPLE:',/,19X,'CACO3     50.0446 G/EQ',/,19X
     1,'HCO3-     61.0171 G/EQ',/,19X,'CO3--     30.0046 G/EQ.',//)
```

```
      READ (1,1731) LINE
      READ (LINE,*,ERR=1728) EQ
      EQUIWT=LINE(1:8)
      JSUB(2)=2
      WRITE (1,1712)
 1712 FORMAT (//,'ELEMENTS DATA BLOCK WILL BE CONSTRUCTED AUTOMATICALLY'
     1,//)
      IF (IELEM.LT.27)GO TO 1004
      WRITE (1,1002)
 1002 FORMAT (1X,52('*'),/,1X,'WARNING:  NUMBER OF ELEMENTS EXCEEDS ',
     1'MAXIMUM POSSIBLE ',/,1X,'CARBON CARD IS DELETED ',/,1X,52('*')/)
      GO TO (1726,1753),JOPT+1
 1004 IELEM=IELEM+1
      TNAME(IELEM)='C'
      NELT(IELEM)=IALK(ISOL)
      TGFW(IELEM)=EQUIWT
      GO TO 1600
 1601 IF (JOPT.EQ.1)GO TO 1753
 1726 IF (IUNITS(ISOL).GE.2.AND.IUNITS(ISOL).LE.3.AND.IELEM.EQ.0)
     1 IREQ(2)=1
      IF (NTOTS(ISOL).EQ.0)GO TO 531
 1320 M=1
 1310 N2=1
C
C        *** LT ***
C
 1326 CHARP='LT'
      FP='I4  '
      CALL QUESTB (M,2,LT(ISOL,M),1,10000,2,*4100)
      IF (.NOT.LIST)GO TO 1057
 1361 CALL LISTM
      GO TO (1326,1356),N2
 1057 N2=2
C
C        *** DTOT ***
C
 1356 CHARP='DTOT'
      FP='A11 '
      CALL QUESTA (M,4,DTOT(ISOL,M),1,2,*4100)
      IF (LIST)GO TO 1361
      M=M+1
      IF (M.LE.NTOTS(ISOL)) GO TO 1310
      WRITE (1,9110)
      WRITE (1,9004) (LT(ISOL,M),DTOT(ISOL,M),M=1,NTOTS(ISOL))
      IF (.NOT.OK(KDUM))GO TO 1320
      GO TO 531
 1725 CONTINUE
C
C   -------------------
C    ELEMENTS DATA BLOCK
C   -------------------
C
      IELEM=IELEM+1
      IF (IOPEN.EQ.0)GO TO 1729
 1536 CALL REF (1,0,0)
      IF (JOPT.EQ.0)GO TO 1530
      WRITE (1,1736) SUB(I)
      WRITE (1,1731)JLINE(1)
      CALL REF (0,0,3)
      GO TO (1530,1531,1531,1536), JOPT+1
 1531 READ (JLINE(1),9102) TNAME(IELEM),NELT(IFLEM),TGFW(IELEM)
      IREQ(2)=0
      IF (JOPT.EQ.1) GO TO 1600
C
C        *** TNAME ***
C
 1729 CHARP='TNAME'
      FP='A8  '
      CALL QUESTA (0,5,TNAME(IELEM),0,3,*4102)
      IF (.NOT.LIST)GO TO 1549
      CALL LISTM
      GO TO 1729
 1549 IF (.NOT.EXIT)GO TO 1550
 1530 IELEM=IELEM-1
      IF (IELEM.EQ.0)JSUB(2)=0
      GO TO 531
 1550 IREQ(2)=0
C
C        *** NELT ***
C
      CHARP='NELT'
      FP='I2  '
      CALL QUESTB (0,4,NELT(IELEM),4,30,2,*4104)
      IF (.NOT.LIST) GO TO 1558
      CALL LISTM
      GO TO 1550
 1558 DO 1547 M=1,IELEM-1
 1547 IF (NELT(IELEM).EQ.NELT(M))GO TO 1548
      GO TO 1570
 1548 WRITE (1,1551) NELT(M)
 1551 FORMAT (/,'WARNING:  ELEMENT #',I2,' IS ALREADY ENTERED.'/)
C
C        *** TGFW ***
C
 1570 CHARP='TGFW'
      FP='A10 '
      CALL QUESTA (0,4,TGFW(IELEM),1,2,*4106)
      IF (.NOT.LIST) GO TO 1580
      CALL LISTM
      GO TO 1570
 1580 WRITE (1,9110)
      WRITE (1,9102) TNAME(IELEM),NELT(IELEM),TGFW(IELEM)
      IF (.NOT.OK(KDUM)) GO TO 1729
C
C           KEEP TRACK OF ELEMENTS AND SPECIES
C
 1600 IF(ICHECK(2,NELT(IELEM)).EQ.1)GO TO 1557
      ICHECK(1,NELT(IELEM))=1
      GO TO 1575
 1557 ICHECK(2,NELT(IFLEM))=0
 1575 IF (I.EQ.1)GO TO 1601
      IF (IELEM.EQ.27) GO TO 531
      IF (IOPEN.NE.0)GO TO 1725
      WRITE (1,1573)
 1573 FORMAT (/,'MORE ELEMENTS?')
      IF (YN(KDUM)) GO TO 1725
      GO TO 531
 1750 CONTINUE
C
C  -----------------
```

```
C  SPECIES DATA BLOCK
C  ------------------
C
      ISPECI=ISPECI+1
      IF (IOPEN.EQ.O)GO TO 1590
 1523 CALL REF (1,O,O)
      IF (JOPT.EQ.O)GO TO 1529
      WRITE (1,1736)SUB(I)
      WRITE (1,1731)JLINE(1)
      READ (JLINE(1),9202) NI(ISPECI)
      CALL REF (3,1,3)
      GO TO (1521,1521,1523),JOPT
      CALL REF (O,O,2)
      IF (JOPT.EQ.2) GO TO 1523
      ISDEL(ISPECI)=1
      GO TO 1750
 1521 READ (JLINE(1),9203) SNAME(ISPECI),NSP(ISPECI),KFLAG
     1(ISPECI),GFLAG(ISPECI),ZSP(ISPECI),THSP(ISPECI),DHA(ISPECI)
     2,ADHSP(ISPECI,1),ADHSP(ISPECI,2),ALKSP(ISPECI)
      READ (JLINE(2),9204) LKTOSP(ISPECI),DHSP(ISPECI),
     1(ASP(ISPECI,MMM),MMM=1,5)
      READ (JLINE(3),9205) (LSP(ISPECI,MMM),CSP(ISPECI,MMM),
     1MMM=1,NSP(ISPECI))
      IF (JOPT.EQ.1) GO TO 1670
C
C       *** I ***
C
 1590 CHARP='I'
      FP='I3  '
      CALL QUESTB (O,1,NI(ISPECI),4,250,1,*4110)
      IF (.NOT.EXIT) GO TO 1654
 1529 ISPECI=ISPECI-1
      IF (ISPECI.EQ.O)JSUB(3)=O
      IF (IOPEN.NE.O)GO TO 531
      GO TO 1933
 1654 WRITE (1,9110)
      WRITE (1,9202) NI (ISPECI)
      IF (.NOT.OK(KDUM)) GO TO 1590
      IF(ISDEL(ISPECI).NE.1) GO TO 1660
      IF (JOPT.EQ.2)GO TO 1750
      GO TO 1934
C
C       *** SNAME ***
C
 1660 CHARP='SNAME'
      FP='A8  '
      CALL QUESTA (O,5,SNAME(ISPECI),O,O,*4112)
C
C          IS IT A MASTER SPECIE....
C
 1670 IMAST=O
      IF (NI(ISPECI).LE.30.AND.NI(ISPECI).GT.3.AND.ISDEL(ISPECI)
     1.NE.1)IMAST=1
      IF (JOPT.EQ.1.AND.IMAST.EQ.O)GO TO 1750
      IF (IMAST.EQ.O.OR.(NFLAG.EQ.1.AND.JOPT.NE.2))GO TO 1676
C
C          KEEP TRACK OF ELEMENTS AND SPECIES...
C
      IF (ICHECK(1,NI(ISPECI)).EQ.1)GO TO 1679
      ICHECK(2,NI(ISPECI))=1
      GO TO 1595
 1679 ICHECK(1,NI(ISPECI))=0
 1595 IF (JOPT.EQ.1)GO TO 1750
C
C         IF IT IS A MASTER SPECIES, A LOT OF VARIABLES CAN BE
C         DETERMINED WITHOUT ASKING THE USER. .
C
      NSP(ISPECI)=1
      KFLAG(ISPECI)=0
      CSP(ISPECI,1)=' 1.0'
      LSP(ISPECI,1)=NI(ISPECI)
      LKTOSP(ISPECI)=' 0.0'
      DHSP(ISPECI)=' 0.0'
      DO 1678 NII=1,5
 1678 ASP(ISPECI,NII)=' 0.0'
      GO TO 1690
C
C        *** NSP ***
C
 1676 CHARP='NSP'
      FP='I3  '
      CALL QUESTB (0,3,NSP(ISPECI),0,6,0,*4114)
C
C        *** KFLAG ***
C
 1680 CHARP='KFLAG'
      FP='I2  '
      CALL QUESTB (0,5,KFLAG(ISPECI),0,1,0,*4116)
C
C        *** GFLAG ***
C
 1690 CHARP='GFLAG'
      FP='I2  '
      CALL QUESTB (0,5,GFLAG(ISPECI),0,1,0,*4118)
C
C        *** ZSP ***
C
 1780 CHARP='ZSP'
      FP='A10 '
      CALL QUESTA (0,3,ZSP(ISPECI),1,0,*4120)
C
C        *** THSP ***
C
 1790 CHARP='THSP'
      FP='A10 '
      CALL QUESTA (0,4,THSP(ISPECI),1,0,*4122)
C
C        *** DHA ***
C
 1880 CHARP='DHA'
      FP='A10 '
      CALL QUESTA (0,3,DHA(ISPECI),1,0,*4124)
      IF (GFLAG(ISPECI).EQ.1)GO TO 1891
      ADHSP(ISPECI,1)=' 0.0'
      ADHSP(ISPECI,2)=' 0.0'
      GO TO 1740
C
C        *** ADHSP ***
C
 1891 M=1
 1892 CHARP='ADHSP'
      FP='A10 '
      CALL QUESTA (M,5,ADHSP(ISPECI,M),1,0,*1897)
      M=M+1
      IF (M.EQ.3)GO TO 1740
      GO TO 1892
 1897 GO TO (4126,4128), M
C
C        *** ALKSP ***
C
 1740 CHARP='ALKSP'
      FP='A10 '
      CALL QUESTA (0,5,ALKSP(ISPECI),1,0,*4130)
      WRITE (1,9110)
      WRITE (1,9203)SNAME(ISPECI),NSP(ISPECI),KFLAG(ISPECI),
     1GFLAG(ISPECI),ZSP(ISPECI),THSP(ISPECI),DHA(ISPECI),
     2ADHSP(ISPECI,1),ADHSP(ISPECI,2),ALKSP(ISPECI)
      IF (.NOT.OK(KDUM)) GO TO 1660
 1960 IF(IMAST.EQ.0)GO TO 1967
      GO TO 1930
C
C        *** LKTOSP ***
C
 1967 CHARP='LKTOSP'
      FP='A10 '
      CALL QUESTA (0,6,LKTOSP(ISPECI),1,0,*4132)
C
C        *** DHSP ***
C
 1970 CHARP='DHSP'
      FP='A10 '
      CALL QUESTA (0,4,DHSP(ISPECI),1,0,*4136)
      IF (KFLAG(ISPECI).EQ.1)GO TO 1986
C
C        *** ASP ***
C
      DO 1988 K=1,5
 1988 ASP(ISPECI,K)=' 0.0'
      GO TO 1990
 1986 K=1
 1987 CHARP='ASP'
      FP='A12 '
      CALL QUESTA (K,3,ASP(ISPECI,K),1,0,*4138)
      K=K+1
      IF (K.LT.6)GO TO 1987
 1990 WRITE (1,9110)
      WRITE (1,9204) LKTOSP(ISPECI),DHSP(ISPECI),(ASP(ISPECI,I8),
     1I8=1,5)
      IF (.NOT.OK(KDUM)) GO TO 1960
 1910 K=1
      IF (NSP(ISPECI).EQ.0)GO TO 1930
 1912 K2=1
C
C        *** LSP, CSP ***
C
 1915 IF (K2.EQ.1) THEN
        CHARP='LSP'
        FP='I3  '
        CALL QUESTB (K,3,LSP(ISPECI,K),1,30,2,*4142)
      ELSEIF (K2.EQ.2) THEN
```

```
        CHARP='CSP'
        FP='A7  '
        CALL QUESTA (K,3,CSP(ISPECI,K),1,2,*4144)
      ENDIF
      IF (.NOT.LIST)GO TO 1922
      CALL LISTM
      GO TO 1915
 1922 IF (K2.EQ.2) GO TO 1923
      K2=2
      GO TO 1915
 1923 K=K+1
      IF (K.GT.NSP(ISPECI)) GO TO 1940
      GO TO 1912
 1940 WRITE (1,9110)
      WRITE (1,9205)(LSP(ISPECI,MM),CSP(ISPECI,MM),MM=1,NSP(ISPECI))
      IF (.NOT.OK(KDUM))GO TO 1910
 1930 IF (IOPEN.NE.0)GO TO 1750
      WRITE (1,1931)
 1931 FORMAT (/,'MORE SPECIES?')
      IF (YN(KDUM))GO TO 1750
 1933 WRITE (1,1932)
 1932 FORMAT (/,'ANY SPECIES TO DELETE?')
 1936 IF (.NOT.YN(KDUM))GO TO 531
      ISDEL(ISPECI+1)=1
      JSUB(3)=1
      GO TO 1750
 1934 WRITE (1,1935)
 1935 FORMAT (/,'MORE SPECIES TO DELETE?')
      GO TO 1936
C
C     -------------------
C     MINERALS DATA BLOCK
C     -------------------
C
 3260 CONTINUE
      IF (IMINO.EQ.0.OR.IOPEN.NE.0)GO TO 3100
C
C         MINERAL DATA AVAILABLE...
C
      WRITE (1,3002)
 3002 FORMAT (/,'PRE-CONSTRUCTED MINERAL DATA ARE AVAILABLE.'/,
     1'DO YOU WISH TO HAVE ANY OF THEM?')
      IF (.NOT.YN(KDUM))GO TO 3100
C
C         PRINT THE LIST OF MINERALS.....
C
 3004 WRITE(1,3003)(K,MNAMEO(K),K=1,IMINO)
 3003 FORMAT (/20(1X,5(I3,1X,A8,2X,:)/))
 3021 WRITE (1,3005)
 3005 FORMAT (/,'ENTER THE INDEX NUMBER OF MINERAL. (TYPE <STOP> TO'
     1,' EXIT)')
      READ (1,1731) LINE
      IF (LINE(1:4).EQ.'STOP'.OR.LINE(1:4).EQ.'stop') GO TO 3010
      READ (LINE,*,ERR=3004) INDEX
      IF (INDEX.GT.IMINO.OR.INDEX.LT.1)GO TO 3004
      IF (MUSED(INDEX).EQ.1)GO TO 3012
      MUSED(INDEX)=1
      GO TO 3013
 3012 WRITE (1,3014) INDEX
 3014 FORMAT (//,'MINERAL # ',I3,' HAS ALREADY BEEN ENTERED.'//)
```

```
      GO TO 3021
 3013 IMIN(1)=IMIN(1)+1
      IM=IMIN(1)
      IREQ(4)=0
      MNAME(1,IM)=MNAMEO(INDEX)
      NMINO(1,IM)=NMINOO(INDEX)
      THMIN(1,IM)=THMINO(INDEX)
      LKTOM(1,IM)=LKTOMO(INDEX)
      DHMIN(1,IM)=DHMINO(INDEX)
      MFLAG(1,IM)=MFLAGO(INDEX)
      SIMIN(1,IM)=SIMINO(INDEX)
      DO 3006 K2=1,NMINO(1,IM)
      LMIN(1,IM,K2)=LMINO(INDEX,K2)
 3006 CMIN(1,IM,K2)=CMINO(INDEX,K2)
 3015 LFLAG=1
      GO TO 3032
 3020 DO 3008 K2=1,5
 3008 AMIN(1,IM,K2)=AMINO(INDEX,K2)
      GO TO 3210
 3024 IF (MFLAG(II,IM).EQ.1) GO TO 3020
 3000 IF (OK(KDUM)) GO TO 3016
      WRITE (1,3017)
 3017 FORMAT ('DO YOU WISH TO CHANGE SIMIN?')
      IF (.NOT.YN(KDUM))GO TO 3019
      LFLAG=3
      GO TO 3167
 3009 WRITE (1,3022)
 3022 FORMAT ('DO YOU WISH TO CHANGE ANYTHING ELSE?')
      IF (.NOT.YN(KDUM))GO TO 3015
 3019 LFLAG=2
      GO TO 3102
 3016 LFLAG=0
      GO TO 3021
 3010 WRITE (1,3011)
 3011 FORMAT (/,'MORE MINERALS TO BE TYPED IN FROM THE TERMINAL?')
      IF (.NOT.YN(KDUM)) GO TO 3061
 3100 IF (IOPEN.EQ.0)GO TO 3221
      IMIN(II)=IMIN(II)+1
      IM=IMIN(II)
 3062 CALL REF (1,0,0)
      IF (JOPT.NE.0)GO TO 3056
 3059 IMIN(II)=IMIN(II)-1
 3061 IF (IMIN(II).EQ.0)JSUB(I)=0
      GO TO 531
 3056 WRITE (1,1736) SUB(I)
      WRITE (1,1731)JLINE(1)
       READ (JLINE(1),9302)MNAME(II,IM),NMINO(II,IM),THMIN(II,IM)
     1,LKTOM(II,IM),DHMIN(II,IM),MFLAG(II,IM),SIMIN(II,IM)
      IF (MNAME(II,IM).NE.DELETE)GO TO 3051
      CALL REF (0,0,2)
      GO TO (3063,3062),JOPT
 3063 IDELET=1
      GO TO 3062
 3051 NLINE=2
      IF (NMINO(II,IM).GT.5)NLINE=3
      IF (MFLAG(II,IM).NE.1)NLINE=NLINE-1
      CALL REF (NLINE,1,3)
      READ (JLINE(1),9303)(LMIN(II,IM,MMM),CMIN(II,IM,MMM),MMM=1,5)
      IF (NMINO(II,IM).LE.5)GO TO 3054
      READ (JLINE(2),9303)(LMIN(II,IM,MMM),CMIN(II,IM,MMM),MMM=6
     1,NMINO(II,IM))
 3054 IF (MFLAG(II,IM).NE.1)GO TO 3057
      READ (JLINE(NLINE),9304) (AMIN(II,IM,MMM),MMM=1,5)
 3057 GO TO (3102,3062), JOPT-1
      IREQ(I)=0
      GO TO 3100
C
C        *** MNAME ***
C
 3221 IMIN(II)=IMIN(II)+1
      IM=IMIN(II)
      LFLAG=0
 3102 CHARP='MNAME'
      FP='A8  '
      CALL QUESTA (0,5,MNAME(II,IM),0,1,*8000)
      IF (EXIT) GO TO 3059
 3106 IREQ(I)=0
C
C        *** NMINO ***
C
 3110 CHARP='NMINO'
      FP='I2  '
      CALL QUESTB (0,5,NMINO(II,IM),1,10,0,*8002)
C
C        *** THMIN ***
C
 3120 CHARP='THMIN'
      FP='A10 '
      CALL QUESTA (0,5,THMIN(II,IM),1,0,*8004)
C
C        *** LKTOM ***
C
 3130 CHARP='LKTOM'
      FP='A10 '
      CALL QUESTA (0,5,LKTOM(II,IM),1,0,*8006)
C
C        *** DHMIN ***
C
 3140 CHARP='DHMIN'
      FP='A10 '
      CALL QUESTA (0,5,DHMIN(II,IM),1,0,*8008)
C
C        *** MFLAG ***
C
 3150 CHARP='MFLAG'
      FP='A10 '
      CALL QUESTB (0,5,MFLAG(II,IM),0,1,0,*8010)
      IF (LFLAG FQ.2) GO TO 3032
C
C        *** SIMIN ***
C
 3167 CHARP='SIMIN'
      FP='A10 '
      CALL QUESTA (0,5,SIMIN(II,IM),1,0,*8012)
      IF (LFLAG.EQ.3)GO TO 3009
 3032 WRITE (1,9110)
      WRITE (1,9302) MNAME(II,IM),NMINO(II,IM),THMIN(II,IM),LKTOM(II,IM)
     1,DHMIN(II,IM),MFLAG(II,IM),SIMIN(II,IM)
      IF (LFLAG.EQ.1)GO TO 3187
      IF (LFLAG.EQ.2) LFLAG=4
      IF (.NOT.OK(KDUM)) GO TO 3102
      IF (LFLAG.EQ.4) NFLAG=1
C
C        *** LMIN, CMIN ***
C
 3190 K=1
 3192 K2=1
 3195 IF (K2.EQ.1) THEN
        CHARP='LMIN'
        FP='I4  '
        CALL QUESTB (K,4,LMIN(II,IM,K),0,0,2,*8014)
      ELSEIF (K2.EQ.2) THEN
        CHARP='CMIN'
        FP='A11 '
        CALL QUESTA (K,4,CMIN(II,IM,K),1,2,*8016)
      ENDIF
      IF (.NOT.LIST)GO TO 3191
      CALL LISTM
      GO TO 3195
 3191 IF (K2.EQ.2) GO TO 3186
      K2=2
      GO TO 3195
 3186 K=K+1
      IF (K.LE.NMINO(II,IM)) GO TO 3192
      WRITE (1,9110)
 3187 WRITE (1,9303) (LMIN(II,IM,K),CMIN(II,IM,K),K=1,NMINO(II,IM))
      IF (LFLAG.EQ.1) GO TO 3024
      IF (.NOT.OK(KDUM)) GO TO 3190
      IF(MFLAG(II,IM).EQ.1)GO TO 3201
      IF (LFLAG.EQ.4) GO TO 3016
      IF (IOPEN.NE.0)GO TO 3100
      GO TO 3010
C
C        *** AMIN ***
C
 3201 IF (LFLAG.EQ.4) NFLAG=1
 3200 K=1
 3207 CHARP='AMIN'
      FP='A12 '
      CALL QUESTA (K,4,AMIN(II,IM,K),1,0,*8018)
      K=K+1
      IF (K.LT.6)GO TO 3207
      WRITE (1,9110)
 3210 WRITE (1,9304)(AMIN(II,IM,K),K=1,5)
      IF (LFLAG.EQ.1) GO TO 3000
      IF (.NOT.OK(KDUM)) GO TO 3200
      IF (LFLAG.EQ.4) GO TO 3016
      IF (IOPEN.NE.0)GO TO 3100
      GO TO 3010
 3250 CONTINUE
C
C     ------------------
C     LOOK MIN DATA BLOCK
C     ------------------
C
      IF(IMIN(2).NE.0.OR.IOPEN.NE.0)GO TO 3100
      WRITE (1,3251)
 3251 FORMAT (/,'DO YOU WANT TO DELETE ALL OLD MINERALS?')
      IF (YN(KDUM))IDELET=1
      IF (IDELET.EQ.1) JSUB(I)=1
```

```
C
C           SINCE LOOK MIN IS ALMOST IDENTICAL TO MINERAL,
C           WHY NOT USE MINERAL SECTION AND SAVE SOME SPACE?
C
      GO TO 3100
 3270 CONTINUE
C
C     ---------------
C     TEMP DATA BLOCK
C     ---------------
C
      IF(IOPT(4).EQ.0)GO TO 3320
      NTEMP=IOPT(4)
      IF (IOPT(4).EQ.3)NTEMP=NSTEPS
      IF (IOPEN.EQ.0)GO TO 3308
      READ (13,9501)(XTEMP(K3),K3=1,NTEMP)
      WRITE (1,1736) SUB(I)
      WRITE (1,9501)(XTEMP(K3),K3=1,NTEMP)
      CALL REF (0,0,1)
      IF (JOPT.NE.1) GO TO 3308
      IREQ(6)=0
      GO TO 531
C
C       *** XTEMP ***
C
 3308 K=1
 3307 CHARP='XTEMP'
      FP='A10 '
      CALL QUESTA (K,5,XTEMP(K),1,1,*8020)
      IF (.NOT.EXIT)GO TO 3312
      JSUB(6)=0
      GO TO 531
 3312 K=K+1
      IF (K.LE.NTEMP)GO TO 3307
      IREQ(6)=0
      WRITE (1,9110)
      WRITE (1,9501)(XTEMP(K),K=1,NTEMP)
      IF (OK(KDUM))GO TO 531
      GO TO 3308
 3320 WRITE (1,3321)
 3321 FORMAT (/,'ERROR:  TEMP DATA BLOCK NOT REQUIRED WHEN IOPT(4) ='
     1,' 0',//)
      JSUB(6)=0
      GO TO 531
 3280 CONTINUE
C
C     ----------------
C     STEPS DATA BLOCK
C     ----------------
C
      IF(IOPT(3).EQ.0.OR.IOPT(3).EQ.5.OR.IOPT(3).EQ.6)GO TO 3630
      NSTEP=NSTEPS
      IF (IOPT(3).EQ.4)NSTEP=1
      IF (IOPEN.EQ.0)GO TO 3608
      READ (13,9501)(XSTEP(K3),K3=1,NSTEP)
      WRITE (1,1736) SUB(I)
      WRITE (1,9501)(XSTEP(K3),K3=1,NSTEP)
      CALL REF (0,0,1)
      GO TO (3801,3801,3608), JOPT
 3801 IREQ(7)=0
```

```
      IF (JOPT.NE.2) GO TO 531
C
C        *** XSTEP ***
C
 3608 K=1
 3607 CHARP='XSTEP'
      FP='A10 '
      CALL QUESTA (K,5,XSTEP(K),1,1,*3620)
      IF (.NOT.EXIT)GO TO 3606
      JSUB(7)=0
      GO TO 531
 3606 K=K+1
      IF (K.LE.NSTEP)GO TO 3607
      IREQ(7)=0
      WRITE (1,9110)
      WRITE (1,9501)(XSTEP(K),K=1,NSTEP)
      IF (OK(KDUM))GO TO 531
      GO TO 3608
 3620 GO TO (8022,8024,8026,8028),IOPT(3)
 3630 WRITE (1,3631) IOPT(3)
 3631 FORMAT (/,'ERROR:  STEPS DATA BLOCK NOT ALLOWED WHEN IOPT(3) ='
     1,1X,I1,//)
      JSUB(7)=0
      GO TO 531
 3900 CONTINUE
C
C     -------------------
C     REACTION DATA BLOCK
C     -------------------
C
      IF (NCOMPS.NE.0)GO TO 3902
      WRITE (1,3901)
 3901 FORMAT (//,'ERROR:   REACTION DATA BLOCK NOT ALLOWED WHEN',
     1' NCOMPS = 0',//)
      JSUB(8)=0
      GO TO 531
 3902 IF (IOPEN.EQ.0)GO TO 5010
      READ (13,9701)(LREAC(K3),CREAC(K3),THMEAN(K3),K3=1,NCOMPS)
      WRITE (1,1736) SUB(I)
      WRITE (1,9701)(LREAC(K3),CREAC(K3),THMEAN(K3),K3=1,NCOMPS)
      CALL REF (0,0,1)
      IF (JOPT.EQ.2) GO TO 5010
      IREQ(8)=0
      IF (JOPT.EQ.1) GO TO 531
C
C        *** THMEAN, LREAC, CREAC ***
C
 5010 K=1
 5012 K2=1
 5015 IF (K2.EQ.1) THEN
        CHARP='LREAC'
        FP='I4  '
        CALL QUESTB (K,5,LREAC(K),0,0,3,*8032)
      ELSEIF (K2.EQ.2) THEN
        CHARP='CREAC'
        FP='A8  '
        CALL QUESTA (K,5,CREAC(K),1,3,*8034)
      ELSEIF (K2.EQ.3) THEN
        CHARP='THMEAN'
        FP='A8  '
```

```
         CALL QUESTA (K,6,THMEAN(K),1,3,*8036)
      ENDIF
      IF (.NOT.EXIT)GO TO 5023
 5300 JSUB(8)=0
      GO TO 531
 5023 IF (.NOT.LIST) GO TO 5025
      CALL LISTM
      GO TO 5015
 5025 IF (K2.EQ.3) GO TO 5026
      K2=K2+1
      IREQ(8)=0
      GO TO 5015
 5026 K=K+1
      IF (K.GT.NCOMPS) GO TO 5027
      GO TO 5012
 5027 WRITE (1,9110)
      WRITE (1,9701) (LREAC(K),CREAC(K),THMEAN(K),K=1,NCOMPS)
      IF (OK(KDUM)) GO TO 531
      GO TO 5010
 6000 CONTINUE
C
C     ------------------
C     NEUTRAL DATA BLOCK
C     ------------------
C
      IF(IOPT(2).NE.2)GO TO 6040
      IF (IOPEN.EQ.0)GO TO 6010
      CALL REF (1,1,1)
      GO TO (6100,6110,6110,6010),JOPT+1
 6100 JSUB(9)=0
      GO TO 531
 6110 READ(JLINE(1),9801)LPOS,LNEG
      IREQ(9)=0
      IF (JOPT.EQ.1)GO TO 531
C
C        *** LPOS ***
C
 6010 CHARP='LPOS'
      FP='I5   '
      CALL QUESTB (0,4,LPOS,0,0,3,*8038)
      IF (.NOT.EXIT)GO TO 6016
      JSUB(9)=0
      GO TO 531
 6016 IF (.NOT.LIST)GO TO 6017
      CALL LISTM
      GO TO 6010
 6017 IREQ(9)=0
C
C        *** LNEG ***
C
 6020 CHARP='LNEG'
      FP='I5   '
      CALL QUESTB (0,4,LNEG,0,0,2,*8040)
      IF (.NOT.LIST)GO TO 6030
      CALL LISTM
      GO TO 6020
 6030 WRITE (1,9110)
      WRITE (1,9801)LPOS,LNEG
      IF (OK(KDUM)) GO TO 531
      GO TO 6000
 6040 WRITE (1,6041)
 6041 FORMAT (/,'ERROR:  NEUTRAL DATA BLOCK IS REQUIRED ONLY IF IOPT'
     1,'(2) = 2',//)
      JSUB(9)=0
      GO TO 531
 7000 CONTINUE
C
C     ---------------
C     SUMS DATA BLOCK
C     ---------------
C
      IF(ISUM.NE.0.OR.IOPEN.NE.0)GO TO 7001
C
C         DELETE ALL OLD SUMS....
C
      WRITE (1,7003)
 7003 FORMAT (/,'DO YOU WANT TO DELETE ALL OLD SUMS?')
      IF (YN(KDUM))JDELET=1
 7001 ISUM=ISUM+1
      IF (IOPEN.EQ.0)GO TO 7010
 7116 CALL REF (1,0,0)
      IF (JOPT.EQ.0)GO TO 7111
      WRITE (1,1736) SUB(I)
      WRITE (1,1731)JLINE(1)
      READ (JLINE(1),9901) SUNAME(ISUM),NSUM(ISUM)
      IF (SUNAME(ISUM).NE.DELETE)GO TO 7120
      CALL REF (0,0,2)
      GO TO (7111,7117,7116),JOPT+1
 7117 JDELET=1
      GO TO 7116
 7120 READ (13,9902)(LSUM(ISUM,M3),M3=1,NSUM(ISUM))
      WRITF (1,9902) (LSUM(ISUM,M3),M3=1,NSUM(ISUM))
      CALL REF (0,0,3)
      GO TO (7111,7001,7010,7116),JOPT+1
C
C       *** SUNAME ***
C
 7010 CHARP='SUNAME'
      FP='A8  '
      CALL QUESTA (0,6,SUNAME(ISUM),0,1,*8042)
      IF (.NOT.EXIT)GO TO 7020
 7111 ISUM=ISUM-1
      IF (ISUM.EQ.0)JSUB(10)=0
      GO TO 531
C
C       *** NSUM ***
C
 7020 CHARP='NSUM'
      FP='I2  '
      CALL QUESTB (0,4,NSUM(ISUM),0,50,0,*8044)
      WRITE (1,9110)
      WRITE (1,9901) SUNAME(ISUM),NSUM(ISUM)
      IF (.NOT.OK(KDUM))GO TO 7010
C
C       *** LSUM ***
C
 7030 K=1
 7037 CHARP='LSUM'
      FP='I4  '
      CALL QUESTB (K,4,LSUM(ISUM,K),0,10000,0,*8046)
      K=K+1
      IF (K.LE.NSUM(ISUM))GO TO 7037
      WRITE (1,9110)
      WRITE (1,9902) (LSUM(ISUM,K),K=1,NSUM(ISUM))
      IF (.NOT.OK(KDUM))GO TO 7030
      IF (JOPT.EQ.2)GO TO 7001
      WRITE (1,7051)
 7051 FORMAT (/,'MORE SUMS?')
      IF (YN(KDUM))GO TO 7000
      GO TO 531
C
C  --------------
C  END DATA BLOCK
C  --------------
C
  950 CONTINUE
      JOPT=0
      KKK=1
  954 IF (IREQ(KKK).EQ.1)GO TO 952
  953 KKK=KKK+1
      IF (KKK.EQ.11)GO TO 958
      GO TO 954
C
C         OOPS!!   HE LEFT OUT A DATA BLOCK
C
  952 WRITE (1,955)SUB(KKK)
  955 FORMAT (/,'ERROR:  ',A8,' DATA BLOCK IS REQUIRED'/)
      IERROR=1
      GO TO 953
  958 IF (IERROR.EQ.0)GO TO 957
      JSUB(11)=0
      IERROR=0
      GO TO 531
C
C         EXCLUDE ELEMENTS OR SPECIES THAT ARE ALREADY IN PHREEQE'S
C         THERMODYNAMIC DATA.
C
  957 DO 951 JL=4,30
      IF (ICOL2(JL).EQ.0)GO TO 951
      ICHECK(1,ICOL2(JL))=0
      ICHECK(2,ICOL2(JL))=0
  951 CONTINUE
      JJ=1
  943 JJJ=4
  942 IF (ICHECK(JJ,JJJ).EQ.1)GO TO (944,945),JJ
  949 JJJ=JJJ+1
      IF (JJJ.EQ.31)GO TO 946
      GO TO 942
  946 JJ=JJ+1
      IF (JJ.EQ.3)GO TO 947
      GO TO 943
  944 WRITE (1,948)JJJ
  948 FORMAT ('ERROR:  SPECIES #',I2,' WAS NOT ENTERED.')
  938 IERROR=1
      GO TO 949
  945 WRITE (1,937)JJJ
  937 FORMAT ('ERROR:  ELEMENT #',I2,' WAS NOT ENTERED.')
      GO TO 938
  947 IF (IERROR.EQ.0)GO TO 959
C
```

```
C          HE ISN'T ALLOWED TO END.
C
      IERROR=0
      JSUB(11)=0
      GO TO 531
C
C          EVERYTHING NEEDED IS PRESENT.
C
  959 GO TO 9010
 5001 WRITE (1,5000)
 5000 FORMAT ('MORE SIMULATIONS?')
      IF (.NOT.YN(KDUM))GO TO 50
      IF (JOPEN.EQ.0)GO TO 5003
 5006 READ (13,1731,END=5003)LINE
      WRITE(1,5005)
 5005 FORMAT(/,'DO YOU WISH TO USE THE NEXT SIMULATION IN YOUR',
     1' REFERENCE?')
      IF (.NOT.YN(KDUM))GO TO 5008
      BACKSPACE 13
      IOPEN=1
      GO TO 3
 5008 READ (13,5009,END=5003)LINE
 5009 FORMAT (A3)
      IF (LINE(1:3).EQ.'END')GO TO 5006
      GO TO 5008
 5003 WRITE (1,5002)
 5002 FORMAT (/,'DO YOU WISH TO DEFINE THE PREVIOUS OUTPUT AS '
     1,/,1X,'YOUR NEW REFERENCE?')
      IF (.NOT.YN(KDUM))GO TO 2
C
C          WRITE THE OUTPUT ONTO THE REFERENCE FILE.
C
      OUT=13
      CLOSE (UNIT=13)
      OPEN (UNIT=13,FILE='-REF',STATUS='UNKNOWN')
      REWIND 13
      GO TO 9010
  999 ENDFILE (UNIT=13)
      REWIND 13
      IOPEN=1
C
C          LET'S TRY AGAIN...
C
      GO TO 3
   50 ENDFILE (UNIT=10)
      STOP
C
 9010 CONTINUE
C
C          WRITE TO FILE.....
C
      ITER=1
C
C           PRINT TITLE CARD.
C
      WRITE (OUT,1731)TITLE
C
C          PRINT OPTION CARD.
C
      WRITE (OUT,9991) (IOPT(I),I=1,9),NSTEPS,NCOMPS,VO
 9991 FORMAT (9I1,1X,2I2,6X,A10)
      DO 9999 L=1,11
      IF (JSUB(IORDER(L)).LT.1) GO TO 9999
      IF (IORDER(L).EQ.1)GO TO 9000
      WRITE (OUT,9050)SUB(IORDER(L))
 9050 FORMAT (A8)
      GO TO (9100,9200,9300,9300,9500,9600,9700,9800,9900,9999),IORDER(L
     1)-1
C
C         PRINT SOLUTION DATA BLOCK.
C
 9000 WRITE (OUT,9001) SUB(1),NSOLUT(ITER)
 9001 FORMAT (A8,1X,I1)
      WRITE (OUT,1731) HEAD(ITER)
      WRITE (OUT,9003) NTOTS(ITER),IALK(ITER),IUNITS(ITER),PH(ITER)
     1, PE(ITER),TEMP(ITER),SDENS(ITER)
 9003 FORMAT(I2,I3,I2,3X,4A10)
      IF (NTOTS(ITER).EQ.0)GO TO 9005
      WRITE (OUT,9004)(LT(ITER,M),DTOT(ITER,M),M=1,NTOTS(ITER))
 9004 FORMAT (6(5(I4,A11),:,/))
 9005 IF (ISOL.EQ.ITER) GO TO 9999
      ITER=2
      GO TO 9000
C
C         PRINT ELEMENTS DATA BLOCK.
C
 9100 DO 9103 MM=1,IELEM
 9103 WRITE (OUT,9102) TNAME(MM),NELT(MM),TGFW(MM)
 9102 FORMAT(A8,2X,I2,3X,A10)
      WRITE (OUT,9110)
 9110 FORMAT (1X)
      GO TO 9999
C
C         PRINT SPECIES DATA BLOCK.
C
 9200 DO 9206 MM=1,ISPECI
      WRITE (OUT,9202) NI(MM)
 9202 FORMAT (I3)
      IF(ISDEL(MM).EQ.0)GO TO 9207
      WRITE (OUT,9110)
      GO TO 9206
 9207 WRITE (OUT,9203) SNAME(MM),NSP(MM),KFLAG(MM),GFLAG(MM),ZSP(MM)
     1,THSP(MM),DHA(MM),ADHSP(MM,1),ADHSP(MM,2),ALKSP(MM)
 9203 FORMAT (A8,2X,I3,2I1,6A10)
      WRITE (OUT,9204) LKTOSP(MM),DHSP(MM),(ASP(MM,M),M=1,5)
 9204 FORMAT (2A10,5A12)
      WRITE (OUT,9205)(LSP(MM,M),CSP(MM,M),M=1,NSP(MM))
 9205 FORMAT (6(I3,A7))
 9206 CONTINUE
      WRITE (OUT,9110)
      GO TO 9999
C
C         PRINT MINERALS OR LOOK MIN DATA BLOCK.
C
 9300 NM=IORDER(L)-3
      IF (NM.NE.2.OR.IDELET.NE.1)GO TO 9301
      WRITE (OUT,9050) DELETE
 9301 IM=IMIN(NM)
      DO 9305 MM=1,IM
      WRITE (OUT,9302) MNAME(NM,MM),NMINO(NM,MM),THMIN(NM,MM),LKTOM(NM
     1,MM),DHMIN(NM,MM),MFLAG(NM,MM),SIMIN(NM,MM)
 9302 FORMAT (A8,2X,I2,3X,3A10,5X,I1,9X,A10)
      WRITE (OUT,9303) (LMIN(NM,MM,M),CMIN(NM,MM,M),M=1,NMINO(NM,MM))
 9303 FORMAT (2(5(I4,A11,:),/))
      IF(MFLAG(NM,MM).NE.1)GO TO 9305
      WRITE (OUT,9304) (AMIN(NM,MM,M),M=1,5)
 9305 CONTINUE
      WRITE (OUT,9110)
 9304 FORMAT (5A12)
      GO TO 9999
C
C          PRINT TEMP DATA BLOCK.
C
 9500 WRITE (OUT,9501) (XTEMP(IF),IF=1,NTEMP)
 9501 FORMAT (7(8(A10,:),/))
      GO TO 9999
C
C          PRINT STEP DATA BLOCK.
C
 9600 WRITE (OUT,9501) (XSTEP(IF),IF=1,NSTEP)
      GO TO 9999
C
C          PRINT REACTION DATA BLOCK.
C
 9700 WRITE (OUT,9701)(LREAC(M),CREAC(M),THMEAN(M),M=1,NCOMPS)
 9701 FORMAT (8(4(I4,2A8,:),/))
      GO TO 9999
C
C          PRINT NEUTRAL DATA BLOCK.
C
 9800 WRITE (OUT,9801)LPOS,LNEG
 9801 FORMAT (2I5)
      GO TO 9999
C
C          PRINT SUMS DATA BLOCK.
C
 9900 IF (JDELET.NE.1)GO TO 9904
      WRITE (OUT,9302) DELETE
 9904 DO 9903 MM=1,ISUM
      WRITE (OUT,9901)SUNAME(MM),NSUM(MM)
 9901 FORMAT (A8,2X,I2)
 9903 WRITE (OUT,9902) (LSUM(MM,M),M=1,NSUM(MM))
 9902 FORMAT(20I4)
      WRITE (OUT,9110)
 9999 CONTINUE
C
      IF (OUT.EQ.10) GO TO 5001
      GO TO 999
C
C         HELP MESSAGES....
C
  290 NSTART=N
      GO TO (2000,2020,2040,2060,2080,2100,2120,2140,2160),N
 1000 WRITE (1,1010)
 1010 FORMAT (/1X,'TITLE CARD',2X,'TITLE',/,1X,'FORMAT (A80)',
     1/,1X,'EIGHTY CHARACTERS OF TITLES OR COMMENTS.'//)
      GO TO 10
 2000 WRITE (1,2010) OPTION
 2010 FORMAT (/1X,A11,/,13X,'IOPT(1) = 0, NO PRINT OF',
     1' THERMODYNAMIC DATA OR COEFFICIENTS',/,26X,'OF AQUEOUS',
     2' SPECIES.',//,21X,'= 1, PRINT THE AQUEOUS MODEL DATA',
     3' (WHICH ARE STORED',/26X,'ON DISK) ONCE DURING THE ENTIRE',
     4' COMPUTER RUN.',/,1X,'FORMAT (I1)',//)
      GO TO 91
 2020 WRITE (1,2030) OPTION
 2030 FORMAT(/1X,A11,/,13X,'IOPT(2) = 0, INITIAL SOLUTIONS',
     1' ARE NOT TO BE CHARGE BALANCED.',/,26X,'REACTION SOLUTIONS',
     2' MAINTAIN THE INITIAL CHARGE',/,26X,'IMBALANCE.',//,21X,'= 1,',
     3' PH IS ADJUSTED IN INITIAL SOLUTION(S) TO',/,26X,'OBTAIN CHARGE',
     4' BALANCE.',//,21X,'= 2, THE TOTAL CONCENTRATION OF ONE OF THE',
     5' ELEMENTS',/,26X,'(EXCEPT H OR O) IS ADJUSTED TO OBTAIN',
     6' ELECTRICAL',/,26X,'BALANCE.  NEUTRAL INPUT IS REQUIRED.',/,1X,'F
     7ORMAT (I1)',//)
      GO TO 91
 2040 WRITE (1,2050) OPTION
 2050 FORMAT (/1X,A11,/,13X,'IOPT(3) = 0, NO REACTIONS ARE',
     1' MODELED.  ONLY THE INITIAL',/,26X,'SOLUTIONS ARE SOLVED.'//,
     221X,'= 1, SOLUTION 1 IS MIXED (A HYPOTHETICAL CONSTANT',/,26X,
     3'VOLUME PROCESS) WITH SOLUTION 2 IN SPECIFIED',/,26X,'REACTION',
     4' STEPS.  STEPS INPUT AND A VALUE FOR',/,26X,'NSTEPS ARE REQUIRED'
     5,'.  MINERALS INPUT MAY BE',/,26X,'INCLUDED.',//,21X,'= 2,',
     6' SOLUTION 1 IS TITRATED WITH SOLUTION 2 IN SPECI-',/,26X,
     7'FIED REACTION STEPS.  STEPS INPUT, A VALUE FOR',/,26X,'NSTEPS,',
     8' AND A VALUE FOR VO ARE REQUIRED.',/,26X,'MINERALS INPUT MAY',
     9' BE INCLUDED.',//,21X,'= 3, A',
     !' STOICHIOMETRIC REACTION IS ADDED IN SPECIFIED',/,26X,'REACTION',
     @' STEPS.  REACTION  INPUT, STEPS INPUT,',/,26X,'A VALUE FOR',
     #' NSTEPS, AND A VALUE FOR NCOMPS ARE',/,26X,'REQUIRED.  MINERALS',
     $' INPUT MAY BE INCLUDED.'///' HIT <RETURN> FOR MORE INFORMATION.')
      READ (1,20) LINE
      WRITE(1,2055)
 2055 FORMAT(21X,'= 4, A NET STOICHIOMETRIC',
     ¬' REACTION IS ADDED IN NSTEPS',/,26X,'EQUAL INCREMENTS.  REACTION'
     &,' INPUT, STEPS INPUT,',/,26X,'A VALUE FOR NSTEPS, AND A VALUE FOR
     *' NCOMPS ARE',/,26X,'REQUIRED.  MINERALS INPUT MAY BE INCLUDED.',
     (' ONLY',/,26X,'ONE VALUE FOR THE TOTAL REACTION IS READ IN STEPS
     )',//,21X,'= 5, SOLUTION NUMBER 1 IS EQUILIBRATED WITH MINERAL',
     -/,26X,'PHASES ONLY.  NO OTHER REACTION IS PERFORMED.',/,26X,
     ='MINERALS INPUT IS REQUIRED.',//,21X,'= 6, A REACTION IS ADDED',
     +' TO SOLUTION 1 UNTIL EQUI-',/,26X,'LIBRIUM IS ATTAINED WITH THE',
     ' FIRST PHASE IN',/,26X,'MINERAL INPUT (EQUILIBRIUM WITH OTHER',
     :' MINERALS',/,26X,'PHASES IS MAINTAINED THROUGHOUT THE REACTION)',
     /'.',/,26X,'REACTION INPUT, A VALUE FOR NCOMPS, AND MINERALS',/,
      26X,'INPUT ARE REQUIRED.  NO STEPS INPUT IS REQUIRED.',/,26X,
     ,'NOTE:  THERE SHOULD BE A COMMON ELEMENT IN THE',/,26X,'REACTION',
     `' AND THE FIRST PHASE IN MINERALS INPUT.',/,1X,'FORMAT (I1)',//)
      GO TO 91
 2060 WRITE (1,2070) OPTION
 2070 FORMAT (/1X,A11,/,13X,'IOPT(4) = 0, THE TEMPERATURE OF',
     1' THE REACTION SOLUTION IS',/,26X,'A) THE SAME AS THE INITIAL',
     2' SOLUTION IF ADDING',/,26X,'A REACTION, OR B) CALCULATED LINEARLY
     3 FROM THE',/,26X,'END MEMBERS IF MIXING OR TITRATING.  NO TEMP',
     4/,26X,'INPUT IS REQUIRED.',//,21X,'= 1, THE TEMPERATURE IS',
     5' CONSTANT DURING THE REACTION',/,26X,'STEPS AND DIFFERS FROM THAT
     6 OF THE INITIAL SOL-',/,26X,'UTION(S).  ONE VALUE IS READ IN THE',
     7' TEMP INPUT.'//,21X,'= 2, THE TEMPERATURE IS VARIED FROM T(0) TO'
     8,' T(F) IN',/,26X,'NSTEPS EQUAL INCREMENTS, DURING THE REACTION',/
     9,26X,'STEPS.',//,21X,'= 3, THE TEMPERATURE',
     $' OF EACH REACTION STEP IS SPEC-',/,26X,'IFIED IN TEMP INPUT, IN'
     %,' ORDER.  NSTEPS VALUES',/,26X,'ARE READ.',/,1X,'FORMAT (I1)',//)
```

```
       GO TO 91
 2080 WRITE (1,2090) OPTION
 2090 FORMAT (/1X,A11,/,13X,'IOPT(5) = 0. THE PE FROM THE',
     1' INITIAL SOLUTION IS HELD CON-',/,26X,'STANT DURING ALL THE',
     2' REACTION STEPS FOR THE',/,26X,'SIMULATION.'//,21X,'= 1, THE PE',
     3' OF THE REACTION SOLUTION IS DETERMINED',/,26X,'BY THE REACTION
     4,/,1X,'FORMAT (I1)',//)
       GO TO 91
 2100 WRITE (1,2110) OPTION
 2110 FORMAT (/1X,A11,/,13X,'IOPT(6) = 0. DEBYE-HUCKEL',
     1' ACTIVITY COEFFICIENTS ARE USED FOR',/,26X,'THE CALCULATIONS. ('
     2,'SEE SPECIES INPUT).',//,21X,'= 1, DAVIES ACTIVITY COEFFICIENTS',
     3' ARE USED.  (SEE',/,26X,'SPECIES INPUT)',/,1X,'FORMAT (I1)',//)
       GO TO 91
 2120 WRITE (1,2130) OPTION
 2130 FORMAT (/1X,A11,/,13X,'IOPT(7) = 0. DO NOT SAVE THE',
     1' AQUEOUS PHASE COMPOSITION AT',/,26X,'THE END OF A REACTION FOR',
     2' ADDITIONAL SIMU-',/,26X,'LATIONS.',//,21X,'= 1, SAVE THE FINAL',
     3' REACTION SOLUTION IN SOLUTION',/,26X,'NUMBER 1.',//,21X,'= 2,',
     4' SAVE THE FINAL REACTION SOLUTION IN SOLUTION',/,26X,'NUMBER 2 '
     5,/,1X,'FORMAT (I1)',//)
       GO TO 91
 2140 WRITE (1,2150) OPTION
 2150 FORMAT (/1X,A11,/,13X,'IOPT(8) = 0. THE DEBUGGING PRINT'
     1,' ROUTINE IS NOT CALLED.',//,21X,'= 1, A LONG PRINTOUT IS OUTPUT'
     2,' AT EACH ITERATION IN',/,26X,'EACH PROBLEM.  THIS PRINT IS TO BE
     3 USED ONLY',/,26X,'IF THERE ARE CONVERGENCE PROBLEM WITH THE',
     4/,26X,'PROGRAM.  (SEE SUBROUTINE PBUG)',/,1X,'FORMAT (I1)',//)
       GO TO 91
 2160 WRITE (1,2170) OPTION
 2170 FORMAT (/1X,A11,/,13X,'IOPT(9) = 0. NO PRINTOUT OF EACH',
     1' ARRAY INVERTED.',//,21X,'= 1, A LONG PRINTOUT OCCURS OF THE',
     2' ENTIRE ARRAY TO',/,26X,'BE INVERTED AT EACH ITERATION.  THIS',
     3' PRINT IS',/,26X,'USED ONLY IF THERE ARE CONVERGENCE PROBLEMS ',
     4/,26X,'(SEE SUBROUTINE SLNQ)',/,1X,'FORMAT (I1)',//)
       GO TO 91
 2200 WRITE (1,2210) OPTION
 2210 FORMAT (/1X,A11,/,13X,'NSTEPS',7X,'THE NUMBER OF'
     1,' STEPS.  A VALUE IS',/,26X,'REQUIRED IF IOPT(3) = 1, 2, 3,',
     2'OR 4, OR IF',/,26X,'IOPT(4) = 2 OR 3.',/,1X,'FORMAT (I2)',//)
       GO TO 250
 2300 WRITE (1,2310) OPTION
 2310 FORMAT (/1X,A11,/,13X,'NCOMPS',7X,'THE NUMBER OF CONSTIT',
     1'UENTS IN A NET STOICHIO-',/26X,'METRIC REACTION.  A CONSTITUENT M
     2AY BE ANY',/,26X,'ELEMENT WITH AN INDEX NUMBER BETWEEN 4 AND',
     3/,26X,'30 INCLUSIVE.  NO AQUEOUS SPECIES WITH INDEX',/,26X,'NUMBER
     4S GREATER THAN 30 MAY BE INCLUDED AS',/,26X,'REACTION CONSTITUENTS
     5 EXCEPT H2 AND O2.  ANY',/,26X,'CONSTITUENT WITH AN INDEX NUMBER G
     6REATER THAN',/,26X,'30 IS ASSUMED TO BE EITHER H2 OR O2 AND HAS',/
     7,26X,'THE EFFECT OF RAISING OR LOWERING THE REDOX',/,26X,'STATE OF
     8 THE SOLUTION DEPENDING ON THE AS-',/,26X,'SIGNED VALENCE (THMEAN)
     9.  A VALUE FOR NCOMPS',/,26X,'IS REQUIRED IF IOPT(3) = 3, 4, OR 6
     !',/,1X,'FORMAT (I2)',//)
       GO TO 301
 2400 WRITE (1,2410) OPTION
 2410 FORMAT (/1X,A11,/,13X,'VO',11X,'THE INITIAL VOLUME OF SO',
     1'LUTION NUMBER 1 WHEN',/26X,'MODELING A TITRATION.  THIS UNIT OF V
     2O MUST',/,26X,'BE THE SAME AS THAT OF XSTEP (SEE STEPS INPUT)',/,2
     36X,'IF IOPT(3) = 2.  OTHERWISE, VO IS NOT REQUIRED',/,1X,'FORMAT (
     4F10.5)',//)
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      GO TO 430
 4146 WRITE (1,4147) SUB(1)
 4147 FORMAT (/1X,A8,10X,'THIS INPUT IS USED TO DEFINE A STARTING'
     1,' SOLU-',/,19X,'TION.',//)
      GO TO 621
 4148 WRITE (1,4149) SUB(2)
 4149 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE NAMES AND INDICES',
     1' OF ALL',/,19X,'ELEMENTS IN THE AQUEOUS MODEL DATA BASE.',//)
      GO TO 621
 4150 WRITE (1,4151) SUB(3)
 4151 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE NAMES, INDEX NUMB'
     1'ERS AND',/,19X,'COMPOSITION OF ALL AQUEOUS SPECIES IN THE',
     2' AQUEOUS',/,19X,'MODEL DATA BASE.',//)
      GO TO 621
 4152 WRITE (1,4153) SUB(4)
 4153 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE PHASES WHICH WILL'
     1,' BE MAIN-',/,19X,'TAINED AT EQUILIBRIUM WITH EACH OF THE'
     2,' REACTION',/,19X,'SOLUTIONS',//)
      GO TO 621
 4154 WRITE (1,4155) SUB(5)
 4155 FORMAT (/1X,A8,10X,'THE PURPOSE OF THIS INPUT IS SIMPLY TO '
     1,'PROVIDE',/,19X,'INFORMATION ON THE SATURATION STATE OF THE'
     2,' AQUEOUS',/,19X,'PHASE WITH RESPECT TO DESIRED MINERALS.  '
     3,'THE',/,19X,'MINERALS IN THIS BLOCK OF INPUT DO NOT AFFECT'
     4,' THE',/,19X,'CALCULATIONS OF THE INITIAL SOLUTION OR ANY '
     5,'OF THE',/,19X,'REACTION SOLUTIONS.  THIS INPUT IS NEVER'
     6,' MANDATORY.',//)
      GO TO 621
 4156 WRITE (1,4157) SUB(6)
 4157 FORMAT (/1X,A8,10X,'THIS INPUT VARIES THE TEMPERATURE DURING'
     1,' THE',/,19X,'REACTION STEPS.',//)
      GO TO 621
 4158 WRITE (1,4159) SUB(7)
 4159 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE STEPS OF THE '
     1,'REACTION PROCESS.',//)
      GO TO 621
 4160 WRITE (1,4161) SUB(8)
 4161 FORMAT (/1X,A8,10X,'THIS INPUT DESCRIBES THE STOICHIOMETRY'
     1,' AND VALENCE',/,19X,'OF THE ELEMENTS TO BE ADDED AS A'
     2,' REACTION.',//)
      GO TO 621
 4162 WRITE (1,4163) SUB(9)
 4163 FORMAT (/1X,A8,10X,'THIS INPUT DEFINES THE ELEMENTS TO BE '
     1,'USED TO',/,19X,'ADJUST THE INITIAL SOLUTION(S) TO ELECTRI'
     2,'CAL',/,19X,'NEUTRALITY.',//)
      GO TO 621
 4164 WRITE (1,4165) SUB(10)
 4165 FORMAT (/1X,A8,10X,'THIS INPUT SUMS MOLALITIES OF AQUEOUS'
     1,' SPECIES WHICH',/,19X,'ARE THEN PRINTED IN THE OUTPUT OF THE'
     2,' RUN.  THESE',/,19X,'SUMS DO NOT AFFECT THE CALCULATIONS IN'
     3,' ANY WAY AND',/,19X,'ARE NEVER MANDATORY.',//)
      GO TO 621
 4166 WRITE (1,4167) SUB(11)
 4167 FORMAT (/1X,A8,10X,'THIS CARD TERMINATES INPUT OPERATIONS'
     1,' FOR A',/,19X,'SINGLE SIMULATION.  ANY COMPUTER RUN HAS '
     2,'AT LEAST ONE',/,19X,'END CARD.',//)
      GO TO 621
 4200 WRITE (1,4210)
 4210 FORMAT (/1X,'POSSIBLE KEYWORDS:',//1X,'(1)ELEMENTS, (2)SPECIES'
     1,', (3)SOLUTION, (4)MINERALS, (5)LOOK MIN,',/,1X,'(6)TEMP, '
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    2,'(7)STEPS, (8)REACTION, (9)NEUTRAL, (10)SUMS, (11)END',//,1X
    3,'FORMAT (A8)',//,' FOR MORE INFORMATION ON ANY OF THE DATA'
    4,' BLOCK, ENTER THE',/,1X,'NUMBER ASSOCIATED WITH IT.',/)
     GO TO 621
1492 WRITE (1,1493)SUB(1)
1493 FORMAT (/1X,A8,/,13X,'N',12X,'A NUMBER OF EITHER 1 OR 2 INDICAT'
    1,'ING THE',/,26X,'SOLUTION NUMBER OF THE FOLLOWING DATA.',/,1X
    2,'FORMAT (I1)'//)
     GO TO 1739
4300 WRITE (1,4310) SUB(1)
4310 FORMAT (/1X,A8,/,13X,'HEAD',/,13X,'FORMAT (A80)',/,13X,
    1'TITLE OR COMMENTS ABOUT THE SOLUTION.',//)
     GO TO 1488
4320 WRITE (1,4330) SUB(1)
4330 FORMAT (/1X,A8,/,13X,'NTOTS',8X,'THE NUMBER OF TOTAL CONCENTRATION
    1S TO BE',/,26X,'READ FROM CARD INPUT.  FOR EXAMPLE, IF THE',/,26X,
    2'STARTING SOLUTION IS MGCL2-NAHCO3 SOLUTION',/,26X,'NTOTS = 4 (FOR
    3 MG, CL, NA, AND C)',/,1X,'FORMAT (I2)',//)
     GO TO 1713
4340 WRITE (1,4350) SUB(1)
4350 FORMAT (/1X,A8,/,13X,'IALK',9X,'FLAG WHICH INDICATES WHETHER TOTAL
    1 CARBON OR',/,26X,'TOTAL ALKALINITY IS TO BE INPUT.',//,21X,'= 0,
    2INDICATES THE TOTAL CONCENTRATION OF CARBON',/,26X,'(NOT ALKALINIT
    3Y) IS INPUT IN THE UNITS',/,26X,'SPECIFIED BY IUNITS.',//,21X,'= N
    4, 4<=N<=30, WHERE N IS THE INDEX NUMBER FOR',/,26X,'THE ELEMENT CA
    5RBON, (IN OUR DATA BASE N=15)',/,26X,'INDICATES TOTAL ALKALINITY I
    6S BEING ENTERED.',/,26X,'ELEMENTS INPUT MAY BE REQUIRED.  THE UNIT
    7S OF',/,26X,'ALKALINITY ARE SPECIFIED BY IUNITS',/,26X,'AND IF ',
    9'IUNITS > 0, THE GRAM FORMULA WEIGHT (GFW)',/,26X,'OF THE ELEMENT'
    !,' CARBON IS CRITICALLY IMPORTANT.',/,26X,'THE GFW IN THE CASE OF'
    @,' ALKALINITY MUST BE THE',/,26X,'GRAM EQUIVALENT WEIGHT (GRAMS/EQ
    #UIVALENT) OF',/,26X,'THE CHEMICAL SPECIES IN WHICH THE ALKALINITY',
    $/,26X,'IS REPORTED.  THE FOLLOWING IS A LIST OF',///,' HIT <RETURN
    /> FOR MORE EXPLANATION')
     READ (1,1731) LINE
     WRITE (1,4355)
4355 FORMAT(//26X,'SPECIES ',
    %'COMMONLY USED FOR REPORTING ALKA-',/,26X,'LINITY AND THEIR CORRES
    ¬PONDING EQUIVALENT',/,26X,'WEIGHTS:',//,31X,'CACO3',4X,'50.0446 G/
    &EQ',//,31X,'HCO3-',4X,'61.0171 G/EQ',//,31X,'CO3--',4X,'30.0046 G/
    *EQ',//,26X,'IN OUR DATA BASE 44.010 IS THE GFW OF CARBON',/,26X,'W
    (HICH IS SUITABLE FOR ENTERING CARBON AS',/,26X,'TOTAL CO2.  THIS G
    )FW MUST BE CHANGED VIA',/,26X,'ELEMENTS INPUT IF ALKALINITY IS TO'
    -,' BE ENTERED',/,26X,'AS MG/L OR PPM (IUNITS = 2 OR 3).  IF IUNITS
    =',/,26X,'= 0 ALKALINITY MUST BE INPUT AS EQ/KG H2O AND',/,26X,'IN'
    +,' THIS CASE THE GFW NEED NOT BE CHANGED SINCE',/,26X,'NO CONVERSI
    :ON IS NECESSARY.',/,1X,'FORMAT (I3)',//)
     GO TO (1714,1752),JUMP+1
4360 WRITE (1,4370) SUB(1)
4370 FORMAT (/1X,A8,/,13X,'IUNITS',7X,'FLAG DESCRIBING UNITS OF INPUT C
    1ONCENTRATIONS.',/,26X,'THE PROGRAM MAKES ALL OF ITS CALCULATIONS'
    2,/,26X,'IN TERMS OF MOLALITY AND ANY OTHER ALLOWED',/,26X,'CONCEN'
    3,'TRATION UNITS (MMOLES/L, MG/L,',/26X,'OR PPM) MUST BE CONVERTED'
    4,' TO MOLALITY',/26X,'BEFORE THE CALCULATION MAY BEGIN.  TO MAKE',
    5/26X,'THE CONVERSIONS IT IS NECESSARY TO KNOW THE',/26X,'GRAM FORM
    6ULA WEIGHT (GFW), IN G/MOLE, OF THE',/26X,'CHEMICAL FORMULA IN WHI
    7CH ELEMENTAL ANALYSES',/,26X,'ARE REPORTED.  THE GFW IS AN INPUT P
    8ARAMETER',/,26X,'UNDER ELEMENTS INPUT AND MUST BE IN AGREEMENT',
    9/,26X,'WITH THE ANALYTICAL UNITS FOR EACH SOLUTION',/,26X,'DATA SE
    !T.  (IF THE UNITS ARE MOLALITY, NO',/,26X,'CONVERSION IS NECESSARY
     @ AND THE GFWS ARE NOT',/,26X,'USED.)  NOTE:  ALL ELEMENTS MUST HAV
     #E',/,26X,'THE SAME UNITS.  IT IS NOT POSSIBLE TO ENTER MG/L',/,26X
     $,'OF ONE ELEMENT AND MOLALITY OF ANOTHER.',///,' HIT <RETURN> FOR'
     /,' MORE EXPLANATION')
      READ (1,1731) LINE
      WRITE (1,4375)
 4375 FORMAT (/21X,'= 0, CONCENTRATION ',
     %'OF ELEMENTS ENTERED AS MOLALITY',/,26X,'OF EACH ELEMENT, OR FO','
     ¬R ALKALINITY, EQUIV-',/,26X,'ALENTS/KG H2O.',//,21X,'= 1, CONCENTR
     &ATION OF ELEMENTS ENTERED AS MMOLES/L',/,26X,'OF EACH ELEMENT, OR'
     *,' FOR ALKALINITY, MEQ/L.',//,21X,'= 2, CONCENTRATION OF ELEMENTS
     (ENTERED AS MG/L',/,26X,'OF THE SPECIES WHICH HAS A GRAM FORMULA',
     )/,26X,'WEIGHT GIVEN IN ELEMENTS INPUT.  (ELEMENTS',/,26X,'INPUT MA
     -Y BE REQUIRED.)',//,21X,'= 3, CONCENTRATION OF ELEMENTS ENTERED AS
     = PPM',/,26X,'OF THE SPECIES WHICH HAS A GRAM FORMULA',/,26X,'WEIGH
     +T GIVEN IN ELEMENTS INPUT.  (ELEMENTS',/,26X,'INPUT MAY BE REQUIRE
     :D.)',/,1X,'FORMAT (I1)',//)
      GO TO 1715
 4380 WRITE (1,4390) SUB(1)
 4390 FORMAT (/1X,A8,/,13X,'PH',11X,'THE PH OF THE SOLUTION (THE APPROXI
     1MATE PH',/,26X,'IF IOPT(2) = 1)',/,1X,'FORMAT (F10.3)',//)
      GO TO 1718
 4400 WRITE (1,4410) SUB(1)
 4410 FORMAT (/1X,A8,/,13X,'PE',11X,'THE PE OF THE SOLUTION. REQUIRED FO
     1R ALL',/,26X,'SOLUTIONS.',/,1X,'FORMAT (F10.3)',//)
      GO TO 1723
 4420 WRITE (1,4430) SUB(1)
 4430 FORMAT (/1X,A8,/,13X,'TEMP',9X,'THE TEMPERATURE OF THE SOLUTION IN
     1 DEGREES',/,26X,'CELCIUS.',/,1X,'FORMAT (F10.3)',//)
      GO TO 1724
 4440 WRITE (1,4450) SUB(1)
 4450 FORMAT (/1X,A8,/,13X,'SDENS',8X,'THE DENSITY OF THE SOLUTION ',/,1
     1X,'FORMAT (F10.3)',//)
      GO TO 1482
 4100 WRITE (1,4101) SUB(1)
 4101 FORMAT (/1X,A8,/,13X,'LT,DTOT',6X,'TOTAL CONCENTRATIONS OF ELEMENT
     1S.',/,26X,'LT',8X,'INDEX NUMBER OF THE ELEMENT.',//,26X,'DTOT',
     26X,'TOTAL CONCENTRATION OF THE ELEMENT IN',/,36X,'MOLALITY, MMOLES
     3/L, MG/L, OR',/,36X,'PPM ACCORDING TO IUNITS.',/,1X,'FORMAT (I4'
     4,',1X,F11.4)')
      WRITE (1,4000)
      GO TO (1326,1356),N2
 4102 WRITE (1,4103) SUB(2)
 4103 FORMAT (/1X,A8,/,13X,'TNAME',8X,'ALPHANUMERIC NAME OF ELEMENT.',
     1/,1X,'FORMAT (A8)')
      WRITE (1,4000)
 4000 FORMAT (' NOTE:  FOR A LISTING OF MASTER SPECIES AND ELEMENTS,'
     1,/,8X,'ENTER <LIST>.',//)
      GO TO 1729
 4104 WRITE (1,4105) SUB(2)
 4105 FORMAT (/1X,A8,/,13X,'NELT',9X,'INDEX NUMBER ASSIGNED TO THE ELEME
     1NT.  NUMBER',/,26X,'MUST BE BETWEEN 4 AND 30, INCLUSIVE.',/,1X,
     2'FORMAT (I2)')
      WRITE (1,4000)
      GO TO 1550
 4106 WRITE (1,4107) SUB(2)
 4107 FORMAT (/1X,A8,/,13X,'TGFW',9X,'GRAM FORMULA WEIGHT OF THE SPECIES
     1 USED TO',/,26X,'REPORT THE ANALYTICAL DATA.  IF SOLUTION DATA'
     2,/,26X,'IS TO INCLUDE ALKALINITY, TGFW FOR THE ELEMENT',/,26X,'CAR
     3BON MUST BE THE EQUIVALENT WEIGHT OF THE',/,26X,'REPORTED ALKALINI
     4TY SPECIES.',/,1X,'FORMAT (F10.4)')
      WRITE (1,4000)
      GO TO 1570
 4110 WRITE (1,4111) SUB(3)
 4111 FORMAT (/1X,A8,/,13X,'I',12X,'THE INDEX NUMBER ASSIGNED TO THE AQU
     1EOUS',/,26X,'SPECIES.  NUMBER 4 THROUGH 30 ARE RESERVED',/,26X,
     2'FOR MASTER SPECIES.  250 IS THE MAXIMUM INDEX',/,26X,'NUMBER FOR
     3AN AQUEOUS SPECIES.',/,1X,'FORMAT (I3)',//)
      GO TO 1590
 4112 WRITE (1,4113) SUB(3)
 4113 FORMAT (/1X,A8,/,13X,'SNAME',8X,'ALPHANUMERIC SPECIES NAME.',/,1X,
     1'FORMAT (A8)',//)
      GO TO 1660
 4114 WRITE (1,4115) SUB(3)
 4115 FORMAT (/1X,A8,/,13X,'NSP',10X,'THE TOTAL NUMBER OF MASTER SPECIES
     1 IN THE',/,26X,'ASSOCIATION REACTION THAT FORMS THIS SPECIES;',/,2
     26X,'DO NOT COUNT THE SPECIES ITSELF UNLESS THE',/,26X,'SPECIES IS
     3A MASTER SPECIES.',/,1X,'FORMAT (I3)',//)
      GO TO 1676
 4116 WRITE (1,4117) SUB(3)
 4117 FORMAT (/1X,A8/,13X,'KFLAG',3X,'= 0, THE VAN''T HOFF EXPRESSION IS
     1 USED TO CALCU-',/,26X,'LATE TEMPERATURE DEPENDENCE OF THE ASSOCIA
     2TION',/,26X,'CONSTANT FOR THIS SPECIES.',//,21X,'= 1, AN ANALYTICA
     3L EXPRESSION IS USED TO CALCU-',/,26X,'LATE TEMPERATURE DEPENDENCE
     4 OF THE ASSOCIATION',/,26X,'CONSTANT.',/,1X,'FORMAT (I1)',//)
      GO TO 1680
 4118 WRITE (1,4119) SUB(3)
 4119 FORMAT (/1X,A8,/,13X,'GFLAG',3X,'= 0, THE EXTENDED DEBYE-HUCKEL OR
     1 DAVIS EXPRES-',/,26X,'SION (ACCORDING TO IOPT(6)) IS USED TO CALC
     2ULATE',/,26X,'THE ACTIVITY COEFFICIENT FOR THIS SPECIES.',//,21X,
     3'= 1, THE WATEQ DEBYE-HUCKEL EXPRESSION IS USED',/,26X,'TO CALCULA
     4TE THE ACTIVITY COEFFICIENT OF THIS',/,26X,'SPECIES REGARDLESS OF
     5THE VALUE OF IOPT(6)',/,1X,'FORMAT (I1)',//)
      GO TO 1690
 4120 WRITE (1,4121) SUB(3)
 4121 FORMAT (/1X,A8,/,13X,'ZSP',10X,'THE CHARGE ON THIS AQUEOUS SPECIES
     1.',/,1X,'FORMAT (F10.3)',//)
      GO TO 1780
 4122 WRITE (1,4123) SUB(3)
 4123 FORMAT (/1X,A8,/,13X,'THSP',9X,'THE SUM OF THE FORMAL VALENCE OF T
     1HE REDOX',/,26X,'SPECIES IN THIS SPECIES.  (E.G. FESO4 HAS',/,26X,
     2'A THSP = 2 + 6 = 8.)',/,1X,'FORMAT (F10.3)',//)
      GO TO 1790
 4124 WRITE (1,4125) SUB(3)
 4125 FORMAT (/1X,A8,/,13X,'DHA',10X,'THE EXTENDED DEBYE-HUCKEL A O TERM
     1.',/,1X,'FORMAT (F10.3)'//)
      GO TO 1880
 4126 WRITE (1,4127) SUB(3)
 4127 FORMAT (/1X,A8,/,13X,'ADHSP(1)',5X,'THE A(I) TERM FOR THE WATEQ DE
     1BYE-HUCKEL EXPRESSION.',/,1X,'FORMAT (F10.3)',//)
      GO TO 1892
 4128 WRITE (1,4129) SUB(3)
 4129 FORMAT (/1X,A8,/,13X,'ADHSP(2)',5X,'THE B(I) TERM FOR THE WATEQ DE
     1BYE-HUCKEL EXPRESSION.',/,1X,'FORMAT (F10.3)',//)
      GO TO 1892
 4130 WRITE (1,4131) SUB(3)
 4131 FORMAT (/1X,A8,/,13X,'ALKSP',8X,'THE ALKALINITY ASSIGNED TO THIS A
     1QUEOUS SPECIES.',/,1X,'FORMAT (F10.3)',//)
      GO TO 1740
 4132 WRITE (1,4133) SUB(3)
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4133 FORMAT (/1X,A8,/,13X,'LKTOSP',7X,'LOG (K) AT 25 DEGREES CELCIUS',
    1', WHERE',/)
     WRITE (1,4134)
4134 FORMAT (26X,'LOG (K) = A1 + A2*T + A3/T + A4*T¬2 + A5/T¬2')
     WRITE (1,4135)
4135 FORMAT (/1X,'FORMAT (F10.3)'//)
     GO TO 1960
4136 WRITE (1,4137) SUB(3)
4137 FORMAT (/1X,A8,/,13X,'DHSP',9X,'STANDARD ENTHALPY OF THE ASSOCIAT'
    1,'ION REACTION AT',/,26X,'25 DEGREES CELCIUS ( H(R), IN KCAL/'
    2,'MOLE ).',/,1X,'FORMAT (F10.3)',//)
     GO TO 1970
4138 WRITE (1,4139) SUB(3),K,K
4139 FORMAT (/1X,A8,/,13X,'ASP(',I1,')',7X,'A',I1,' OF THE FOLLOWING',
    1' EQUATION:',/)
     WRITE (1,4134)
     WRITE (1,4140)
4140 FORMAT (/1X,'FORMAT (F12.5)')
     GO TO 1987
4142 WRITE (1,4143) SUB(3)
4143 FORMAT (/1X,A8,/,13X,'LSP',10X,'INDEX NUMBER OF MASTER SPECIES.'
    1,/,1X,'FORMAT (I3)')
     WRITE (1,4000)
     GO TO 1915
4144 WRITE (1,4145) SUB(3)
4145 FORMAT (/1X,A8,/,13X,'CSP',10X,'STOICHIOMETRIC COEFFICIENT OF',
    1' MASTER SPECIES',/,26X,'IN THIS AQUEOUS SPECIES.',/,1X,'FORMAT'
    2,' (F7.3)')
     WRITE (1,4000)
     GO TO 1915
8000 WRITE (1,8001) SUB(I)
8001 FORMAT (/1X,A8,/,13X,'MNAME',8X,'ALPHANUMERIC NAME OF MINERAL',/,
    11X,'FORMAT (A8)',//)
     GO TO 3102
8002 WRITE (1,8003) SUB(I)
8003 FORMAT (/1X,A8,/,13X,'NMINO',8X,'NUMBER OF DIFFERENT SPECIES IN TH
    1E MINERAL',/,26X,'DISSOCIATION REACTION (INCLUDING H+, E-, AND',/
    2,26X,'H2O).  NMINO MUST BE LESS THAN OR EQUAL TO 10.',/,1X,
    3'FORMAT (I2)',//)
     GO TO 3110
8004 WRITE (1,8005) SUB(I)
8005 FORMAT (/1X,A8,/,13X,'THMIN',8X,'THE SUM OF THE VALENCES OF THE RE
    1DOX SPECIES',/,26X,'IN THE MINERAL DISSOCIATION REACTION ',/,1X,
    2'FORMAT (F10.3)',//)
     GO TO 3120
8006 WRITE (1,8007)SUB(I)
8007 FORMAT (/1X,A8,/,13X,'LKTOM',8X,'LOG OF THE EQUILIBRIUM CONSTANT'
    1,' AT 25 DEGREES',/,26X,'CELCIUS FOR THE REACTION',/,1X,'FORM AT'
    2,' (F10.3)',//)
     GO TO 3130
8008 WRITE (1,8009) SUB(I)
8009 FORMAT (/1X,A8,/,13X,'DHMIN',8X,'DELTA H(R) (KCAL/MOLE) FOR THE '
    1,'VANT HOFF',/,26X,'EXPRESSION.',/,1X,'FORMAT (F10.3)'//)
     GO TO 3140
8010 WRITE (1,8011) SUB(I)
8011 FORMAT (/1X,A8,/,13X,'MFLAG',3X,'= 0, THE VANT HOFF EXPRESSION IS'
    1,' USED TO CALCU-',/,26X,'LATE THE TEMPERATURE DEPENDENCE OF THE',
    2' EQUIL-',/,26X,'IBRIUM CONSTANT',//,21X,'= 1, THE ANALYTICAL EXP'
    3,'RESSION IS USED TO CALCU-'/,26X,'LATE THE TEMPERATURE DEPENDENCE
    4 OF THE EQUIL-',/,26X,'IBRIUM CONSTANT.',/,1X,'FORMAT (I1)'//)
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      GO TO 3150
 8012 WRITE (1,8013) SUB(I)
 8013 FORMAT (/1X,A8,/,13X,'SIMIN',8X,'SATURATION INDEX (LOG(ION ACTIVI'
     1,'TY PRODUCT/K(SP)))',/,26X,'DESIRED IN THE FINAL SOLUTION.  SIMIN
     2 = 0.0',/,26X,'WOULD PRODUCE EQUILIBRIUM WITH THE MINERAL',/,26X,
     3'WHILE 1.0 WOULD PRODUCE A SOLUTION 10 TIMES',/,26X,'SUPERSATURATE
     4D (SI = 1.0).  THIS VARIABLE IS',/,26X,'USEFUL IN SPECIFYING THE '
     5,'PARTIAL PRESSURE OF',/,26X,'A GAS.  THE HENRY(S) LAW CONSTANT ',
     6'FOR THE GAS',/,26X,'WOULD BE ENTERED USING THE VANT HOFF (LKTOM)
     7',/,26X,'OR ANALYTICAL EXPRESSION (AMIN) AND THE LOG OF',/,25X,' THE
     8 PARTIAL PRESSURE WOULD BE ENTERED FOR SIMIN.',/,1X,'FORMAT (F10.3
     9)',//)
      GO TO 3167
 8014 WRITE (1,8015) SUB(I)
 8015 FORMAT (/1X,A8,/,13X,'LMIN',9X,'INDEX NUMBER OF SPECIES (NOT NECE'
     1,'SSARILY MASTER',/,26X,'SPECIES) IN THE DISSOCIATION REACTION ',
     2'FOR',/,26X,'THIS MINERAL',/,1X,'FORMAT (I4)')
      WRITE (1,3800)
      GO TO 3195
 8016 WRITE (1,8017) SUB(I)
 8017 FORMAT (/1X,A8,/,13X,'CMIN',9X,'STOICHIOMETRIC COEFFICIENT OF ',
     1'SPECIES IN',/,26X,'DISSOCIATION REACTION.',/,1X,'FORMAT (F11.3)')
      WRITE (1,3800)
      GO TO 3195
 8018 WRITE (1,8019) SUB(I),K,K
 8019 FORMAT (/1X,A8,/,13X,'AMIN(',I1,')',6X,'A',I1,1X,'OF THE FOLLOWING
     1 MINERAL DISSOCIATION',/,26X,'REACTION:',//,26X,'LOG (K) = A1 +'
     2,' A2*T + A3/T + A4*T¬2 + A5/T¬2',//,26X,'WHERE T IS IN DEGREES',
     3' KELVIN',/,1X,'FORMAT (F12.5)',//)
      GO TO 3207
 8020 WRITE (1,8021) SUB(6)
 8021 FORMAT (/1X,A8,/,13X,'XTEMP',8X,'TEMPERATURE IN DEGREES CELSIUS.'
     1,/,1X,'FORMAT (F10.3)',//)
      GO TO 3307
 8022 WRITE (1,8023) SUB(7)
 8023 FORMAT (/1X,A8,/,13X,'XSTEP',8X,'THE FRACTION OF SOLUTION 1 TO BE'
     1,/,26X,'MIXED WITH SOLUTION 2.')
 8030 WRITE (1,8029)
 8029 FORMAT (1X,'FORMAT (F10.9)',//)
      GO TO 3607
 8024 WRITE (1,8025) SUB(7)
 8025 FORMAT (/1X,A8,/,13X,'XSTEP',8X,'THE VOLUME OF SOLUTION 2 TO',
     1' BE',/,26X,'TITRATED INTO SOLUTION 1.  XSTEP MUST',/,26X,'HAVE'
     2,' THE SAME UNITS AS VO.')
      GO TO 8030
 8026 WRITE (1,8027) SUB(7)
 8027 FORMAT (/1X,A8,/,13X,'XSTEP',8X,'THE MOLES OF REACTION TO BE ',
     1'ADDED',/,26X,'TO SOLUTION 1')
      GO TO 8030
 8028 WRITE (1,8031) SUB(7)
 8031 FORMAT (/1X,A8,/,13X,'XSTEP',8X,'THE TOTAL NUMBER OF MOLES OF'
     1,/,26X,'REACTION TO BE ADDED IN NSTEPS',/,26X,'STEPS.  NSTEPS'
     2,' REACTION SOLUTIONS',/,26X,'WILL BE CALCULATED.  THE I(TH) SOLU-'
     3,/,26X,'TION WILL HAVE I*XSTEP/NSTEPS MOLES',/,26X,'OF REACTION'
     4,' ADDED TO SOLUTION 1.')
      GO TO 8030
 8032 WRITE (1,8033) SUB(8)
 8033 FORMAT (/1X,A8,/,13X,'LREAC',8X,'INDEX NUMBER OF ELEMENT FOR THE'
     1,' REACTION.',/,26X,'LREAC MUST BE BETWEEN 4 AND 30 INCLUSIVE.',/,
     226X,'IF LREAC IS GREATER THAN 30 THE PROGRAM',/,26X,'CONSIDERS',
     3' THIS CONSTITUENT TO BE H2 OR ',/,26X,'O2 AND ONLY USES CREAC',
     4' AND THMEAN',/,26X,'TO CHANGE THE OXIDATION STATE OF THE',/,26X
     5,'REACTION SOLUTION.',/,1X,'FORMAT (I4)')
      WRITE (1,3800)
      GO TO 5015
 8034 WRITE (1,8035) SUB(8)
 8035 FORMAT (/1X,A8,/,13X,'CREAC',8X,'STOICHIOMETRIC COEFFICIENT OF'
     1,' THE ELEMENT',/,26X,'IN THE REACTION',/,1X,'FORMAT (F8.3)')
      WRITE (1,3800)
      GO TO 5015
 8036 WRITE (1,8037) SUB(8)
 8037 FORMAT (/1X,A8,/,13X,'THMEAN',7X,'THE VALENCE OF THE ELEMENT IN'
     1,' THE REACTION.',/,26X,'AN ELEMENT MAY BE INCLUDED MORE THAN',
     2' ONCE IN',/,26X,'A REACTION TO ACCOMODATE DIFFERENT VALENCE',/,
     326X,'STATES OF THE ELEMENT.',/,1X,'FORMAT (F8.3)')
      WRITE (1,3800)
      GO TO 5015
 8038 WRITE (1,8039) SUB(9)
 8039 FORMAT (/1X,A8,/,13X,'LPOS',9X,'INDEX NUMBER OF AN ELEMENT WITH'
     1,' A CATION',/,26X,'MASTER SPECIES.',/,1X,'FORMAT (I5)')
      WRITE (1,3800)
      GO TO 6010
 8040 WRITE (1,8041) SUB(9)
 8041 FORMAT (/1X,A8,/,13X,'LNEG',9X,'INDEX NUMBER OF AN ELEMENT WITH'
     1,' AN ANION',/,26X,'MASTER SPECIES.',/,1X,'FORMAT (I5)')
      WRITE (1,3800)
 3800 FORMAT (1X,'NOTE:  FOR A LISTING OF MASTER SPECIES AND ELEMENTS,'
     1,/,8X,'ENTER <LIST>.',//)
      GO TO 6020
 8042 WRITE (1,8043) SUB(10)
 8043 FORMAT (/1X,A8,/,13X,'SUNAME',7X,'ALPHANUMERIC NAME TO BE PRINT'
     1'ED TO IDENTIFY',/,26X,'THE SUM.',/,1X,'FORMAT (A8)'//)
      GO TO 7010
 8044 WRITE (1,8045) SUB(10)
 8045 FORMAT (/1X,A8,/,13X,'NSUM',9X,'THE NUMBER OF INDEX NUMBER TO BE'
     1,' READ.',/,26X,'NSUM<=50.',/,1X,'FORMAT (I2)'//)
      GO TO 7020
 8046 WRITE (1,8047) SUB(10)
 8047 FORMAT (/1X,A8,/,13X,'LSUM',9X,'INDEX NUMBERS OF SPECIES IN '
     1,'SUM.',/,1X,'FORMAT (I4)'//)
      GO TO 7037
      END
      SUBROUTINE RDFILE(SUB)
C
C          THIS SUBROUTINE READS FROM LOGICAL FILE #11,
C          PRE-CONSTRUCTED MINERAL CARDS; AND FROM LOGICAL FILE #12,
C          THE THERMODYNAMIC DATA OF PHREEQE. THE NECESSARY INFORMATION
C          TO CONSTRUCT A MASTER SPECIES AND ELEMENTS TABLE.
C
      REAL ICOL3(0:30),NOUSE6
      CHARACTER *80 LINE
      CHARACTER *12 THMIN(100),LKTOM(100),DHMIN(100),SIMIN(100)
     1,CMIN(100,10),AMIN(100,5)
      CHARACTER *8 NONE,MNAME(100),SUB(11),ICOL1(0:30),ICOL4(0:30)
     1,SPEC(30),KYWORD,NOUSE2
      COMMON /PT1/ MNAME,THMIN,LKTOM,DHMIN
     1,SIMIN,CMIN,AMIN,SPEC
      COMMON /PT2/ NMINO(100),MFLAG(100),LMIN(100,10)
     1,ICOL2(0:30),OPV(30),ICOL3,IMIN
      COMMON /NEW3/ ICOL1,ICOL4
      DATA NONE/'********'/
C
      LREAD=0
      DO 40 M=1,30
   40 ICOL2(M)=0
      NUM=1
C
C          READ MINERAL CARDS.
C          NOTE:  MAXIMUM NUMBER OF MINERALS IS 100.
C
      OPEN (UNIT=11,FILE='FWSS:PHRQ.MINDAT',STATUS='OLD')
      DO 26 M=1,100
      READ (11,27,END=7)MNAME(M),NMINO(M),THMIN(M),LKTOM(M),DHMIN(M)
     1,MFLAG(M),SIMIN(M)
   27 FORMAT (A8,2X,I2,3X,3A10,5X,I1,9X,A10)
      NO2=NMINO(M)
      IF (NO2.LE.5) GO TO 29
      NO2=5
   29 READ (11,28) (LMIN(M,MO),CMIN(M,MO),MO=NUM,NO2)
   28 FORMAT (5(I4,A11))
      IF (NMINO(M).LE.5.OR.NUM.EQ.6) GO TO 30
      NUM=6
      NO2=NMINO(M)
      GO TO 29
   30 IF (MFLAG(M).NE.1) GO TO 26
      READ (11,31) (AMIN(M,MO),MO=1,5)
   31 FORMAT (5A12)
   26 CONTINUE
    7 IMIN=M-1
C
C               READ THERMODYNAMIC DATA OF PHREEQE.
C          NOTE: THE DATA BLOCKS OF PHREEQE DATA CAN BE ARRANGED
C                IN ANY ORDER.
C
      OPEN (UNIT=12,FILE='FWSS:PHRQ.DATBASE',STATUS='OLD')
   48 READ (12,11) KYWORD
   11 FORMAT (A8)
C
C          READ IS REPEATED UNTIL A KEYWORD IS FOUND.
C
   45 IF (KYWORD.EQ.SUB(2))GO TO 42
      IF (KYWORD.EQ.SUB(3))GO TO 44
      READ (12,43,END=50)LINE
   43 FORMAT (A80)
      READ (LINE,11) KYWORD
      GO TO 45
   46 LREAD=LREAD+1
      IF (LREAD.EQ.2)RETURN
      GO TO 48
C
C          READ SPECIES DATA BLOCK.
C
   44 DO 80 JL=1,250
      READ (12,51) NOUSE1
      IF (NOUSE1.EQ.0)GO TO 46
      READ (12,52)NOUSE2,NOUSE3,NOUSE4,NOUSE5,NOUSE6
   51 FORMAT (I3)
   52 FORMAT (A8,2X,I3,2I1,F10.3,//)
      IF (NOUSE3.GT.6)READ (22,53)
   53 FORMAT (1X)
```

```
      IF (NOUSE1.GT.30)GO TO 80
      SPEC(NOUSE1)=NOUSE2
      OPV(NOUSE1)=NOUSE6
   80 CONTINUE
      GO TO 46
C
C          READ ELEMENTS DATA BLOCK.
C
   42 DO 8 JL=1,50
      READ (12,9)ICOL1(O),ICOL2(O),ICOL3(O),ICOL4(O)
    9 FORMAT (A8,2X,I2,3X,F10.0,5X,A8)
      IF (ICOL2(O).GT.30)GO TO 8
      IF (ICOL2(O).NE.O)GO TO 100
      JCOL=JL-1
      GO TO 46
  100 ICOL1(ICOL2(O))=ICOL1(O)
      ICOL2(ICOL2(O))=ICOL2(O)
      ICOL3(ICOL2(O))=ICOL3(O)
      ICOL4(ICOL2(O))=ICOL4(O)
    8 CONTINUE
*****************************************
* THIS CAN ALSO BE USED AS A BREAK-POINT I.E.
*
*  50 STOP
*****************************************
   50 RETURN
C     ***********
      ENTRY LISTM
C     ***********
C
C          THIS SUBROUTINE FORMATS AND PRINTS A TABLE OF MASTER
C          SPECIES AND ELEMENTS.
C
      DO 200 MO=1,3
      ICOL1(MO)=NONE
      ICOL2(MO)=MO
      ICOL3(MO)=0.0
      ICOL4(MO)=NONE
      OPV(MO)=0.0
  200 CONTINUE
      ICOL3(3)=18.0152
      SPEC(1)='H+      '
      SPEC(2)='E-      '
      SPEC(3)='H2O     '
      WRITE (1,201)
  201 FORMAT (/34X,'INPUT FORMULA',/.34X,'CORRESPONDING',5X,'MASTER',/
     1,1X,'ELEMENTS',5X,'#',9X,'GFW',10X,'TO GFW',9X,'SPECIES',6X,'OPV'
     2,/,1X,8('-'),4X,3('-'),4X,10('-'),4X,14('-'),4X,8('-'),4X,5('-')
     3,/)
      DO 203 MO=1,30
      IF (ICOL2(MO).EQ.O)GO TO 203
      WRITE(1,202)ICOL1(MO),ICOL2(MO),ICOL3(MO),ICOL4(MO),SPEC(MO)
     1,OPV(MO)
  203 CONTINUE
  202 FORMAT (1X,A8,4X,I2,5X,F10.4,8X,A8,6X,A8,4X,SP,F4.1,SS)
      RETURN
      END
C
      SUBROUTINE REF (ILINE,KOPT,JOPEN)
C
```

```
C         THIS SUBROUTINE READS CERTAIN NUMBER OF LINES--ACCORDING
C         TO THE VALUE OF ILINE--FROM THE REFERENCE FILE, PRINTS
C         IT(THEM) ON THE SCREEN, AND, DEPENDING ON THE VALUE OF
C         IOPEN, ASKS A QUESTION CONCERNING THE FATE OF THE LINE(S).
C
C         KOPT:  0 = NO PRINT OF LINES
C                1 = PRINT THE LINES
C         JOPEN: 0 = NO QUESTION ASKED
C              > 0 = QUESTION ASKED
C
      COMMON /REFF/ JOPT,IOPEN
      COMMON /REFF1/ I
      COMMON /NEW2/ JLINE
      CHARACTER *80 JLINE(3),LINE
C
      DO 310 II=1,ILINE
      READ (13,10,END=99) JLINE(II)
   10 FORMAT (A80)
      IF (JLINE(II)(1:10).NE.'          ')GO TO 311
      IF (II.NE.1) GO TO 311
      JOPT=0
      RETURN
  311 IF (KOPT.EQ.0) GO TO 310
      WRITE (1,300) JLINE(II)
  300 FORMAT (A80)
  310 CONTINUE
      IF (JOPEN.EQ.0)RETURN
  402 GO TO (303,400,500,600), JOPEN
  303 WRITE (1,301)
  301 FORMAT ('ENTER OPTION.  (1=KEEP, 2=MODIFY, 3=REPLACE)')
  305 READ (1,300) LINE
      READ (LINE,*,ERR=402) JOPT
      IF (JOPT.LE.0.OR.JOPT.GT.3)GO TO 402
      IF ((JOPT.EQ.3).AND.(JOPEN.EQ.2.OR.JOPEN.EQ.4))GO TO 402
      RETURN
   99 IOPEN=0
      RETURN
  400 WRITE (1,401)
  401 FORMAT ('ENTER OPTION.  (1=KEEP, 2=ELIMINATE)')
      GO TO 305
  500 WRITE (1,501)
  501 FORMAT ('ENTER OPTION.  (1=KEEP, 2=MODIFY, 3=ELIMINATE)')
      GO TO 305
  600 WRITE (1,601)
  601 FORMAT ('ENTER OPTION.  (1=KEEP, 2=REPLACE)')
      GO TO 305
      END
C
      SUBROUTINE SPECL (I)
C
C       THIS SUBROUTINE CHECKS FOR SPECIAL CHARACTERS 'EXIT' AND 'LIST'
C
      COMMON /EE/ EXIT,LIST,JFLAG
      COMMON /NEW1/ LINE
      LOGICAL EXIT,LIST
      CHARACTER *80 LINE
C
      EXIT=.FALSE.
      LIST=.FALSE.
      IF (I.EQ.0) RETURN
      IF ((LINE(1:4).EQ.'LIST'.OR.LINE(1:4).EQ.'list').AND.(I.EQ.2.OR.
     1I.EQ.3)) LIST=.TRUE.
      IF ((LINE(1:4).EQ.'EXIT'.OR.LINE(1:4).EQ.'exit').AND.(I.EQ.1.OR
     1I.EQ.3)) EXIT=.TRUE.
      RETURN
      END
C
      LOGICAL FUNCTION OK(KDUM)
C
C         THIS SUBROUTINE ASKS WHETHER IT IS O K
C
      COMMON /PN/ NFLAG
      LOGICAL ANSWER,YN
C
      WRITE (1,10)
   10 FORMAT ('O.K.?')
      NFLAG=0
      KDUM=1
      OK=.TRUE.
      ANSWER=YN(KDUM)
      IF (ANSWER) RETURN
      NFLAG=1
      OK=.FALSE.
      RETURN
      END
C
C    THIS SUBROUTINE READS CHARACTER AND REAL VALUES FROM THE
C  TERMINAL AND CHECKS TO MAKE SURE THAT THEY ARE ENTERED PROPERLY.
C
      SUBROUTINE QUESTA (J1,L1,STRING,K1,M1,*)
      COMMON /REFF/ JOPT,IOPEN
      COMMON /PN/ NFLAG
      COMMON /EE/ EXIT,LIST,JFLAG
      COMMON /NEW1/ LINE
      COMMON /NEW2/ JLINE
      COMMON /NEW4/ CHAR1,F1
      CHARACTER *(*) STRING
      CHARACTER *80 LINE,JLINE(3)
      CHARACTER *72 QUESTN
      CHARACTER *40 FMT
      CHARACTER *16 CHAR,CHAR1
      CHARACTER *4 F,F1
      CHARACTER *2 FO(16)
      INTEGER IVAL
      LOGICAL EXIT,LIST,NONB
      DATA FO/'1 ','2 ','3 ','4 ','5 ','6 ','7 ','8 ','9 ','10','11'
     1,'12','13','14','15','16' /
      DATA QUESTN /'KEEP THE OLD VALUE? (HIT <RETURN> IF YOU DO; IF NO
     1T, REENTER THE DATA)'/
C
C        K=0 ==> CHARACTER STRING
C        K=1 ==> REAL
C        K=2 ==> INTEGER
C
      IF (F1.EQ.'A80') F1='/A80'
   50 J=J1
      CHAR=CHAR1
      F=F1
      K=K1
      L=L1
      M=M1
  100 IF (J.GT.O.AND.J.LT.10) I=1
      IF (J.GE.10.AND.J.LT.100) I=2
      IF (J.GE.100) I=3
      IF (NFLAG.GT.O.OR.JOPT.EQ.2) GO TO 30
      IF (J.GT.O) GO TO 10
      FMT='(/,''INPUT '',A'//FO(L)//')'
      WRITE (1,FMT) CHAR
      GO TO 300
   10 FMT='(/,''INPUT '',A'//FO(L)//',''('',I'//FO(I)//',''')'')'
      WRITE (1,FMT) CHAR,J
      GO TO 300
   30 IF (J.GT.O) GO TO 40
      FMT='(/,''OLD '',A'//FO(L)//',''='',''//F//',/,A72)'
      IF (K.EQ.2) WRITE (1,FMT) CHAR,IVAL,QUESTN
      IF (K.NE.2) WRITE (1,FMT) CHAR,STRING,QUESTN
      GO TO 300
   40 FMT='(/,''OLD '',A'//FO(L)//',''('',I'//FO(I)//',''')='',''//F//',
     1/,A72)'
      IF (K.EQ.2) WRITE (1,FMT) CHAR,J,IVAL,QUESTN
      IF (K.NE.2) WRITE (1,FMT) CHAR,J,STRING,QUESTN
C
C     READ RESPONSE
C
  300 JFLAG=O
      READ (1,105) LINE
  105 FORMAT(A80)
C
C          JFLAG=O ---> PROPER ENTRY
C          JFLAG=1 ---> EXPLANATION IS ASKED
C          JFLAG=2 ---> A NULL ANSWER
C          JFLAG=3 ---> ANSWER OF WRONG TYPE
C          JFLAG=4 ---> SPECIAL CHARACTERS
C
      IF (LINE(1:2).NE.' ') GO TO 110
      JFLAG=2
  110 IF (LINE(1:1).EQ.'?') JFLAG=1
      CALL SPECL (M)
      IF (EXIT.OR.LIST) JFLAG=4
      IF (JFLAG.NE.O) GO TO 200
      GO TO (140,150,120), K+1
  140 STRING=LINE
      GO TO 200
  120 READ (LINE,*,ERR=130) IVAL
      GO TO 200
  150 READ (LINE,*,ERR=130) G
C
C     MAKE SURE THAT DECIMAL POINT IS PRESENT
C
      NONB=.FALSE.
      DO 155 I2=1,80
      IF (LINE(I2:I2).NE.' ') NONB=.TRUE.
      IF (NONB.AND.LINE(I2:I2).EQ.' ') GO TO 130
      IF (LINE(I2:I2).EQ.'.') GO TO 156
  155 CONTINUE
      GO TO 130
  156 STRING=LINE
      GO TO 200
C
  130 JFLAG=3
  200 IF (JFLAG.EQ.2.AND.(NFLAG.NE.0.OR.JOPT.EQ.2)) GO TO 170
      IF (JFLAG.EQ.4) RETURN
      IF (JFLAG.NE.0) RETURN 1
  170 IF (K.NE.2.OR.IMAX.LE.IMIN) RETURN
      IF (IVAL.GT.IMAX.OR.IVAL.LT.IMIN) RETURN 1
      RETURN
      END
C
      LOGICAL FUNCTION YN(KDUM)
C
C          THIS FUNCTION CHECKS FOR YES OR NO ANSWER
C
      CHARACTER *1 YESNO
C
    5 READ (1,10) YESNO
   10 FORMAT (A1)
      YN=.FALSE.
      IF (YESNO.EQ.'Y'.OR.YESNO.EQ.'y') GO TO 20
      IF (YESNO.EQ.'N'.OR.YESNO.EQ.'n') RETURN
      WRITE (1,30)
   30 FORMAT ('PLEASE ANSWER ''Y'' OR ''N'' ')
      GO TO 5
   20 YN=.TRUE.
      RETURN
      END
C
      SUBROUTINE OPEN(ITIME)
C
C          THIS SUBROUTINE GIVES THE USER A CHOICE OF CHOOSING A
C          REFERENCE FILE OR NOT TO USE IT AT ALL.  IF THE
C          REFERENCE FILE IS DESIRED, IT OPENS THE FILE AND
C          POSITION THE POINTER SO THAT THE PROGRAM CAN USE IT;
C          IF REFERENCE FILE IS NOT WANTED, IT SETS IOPEN TO ZERO
C          AND RETURN TO 'MAIN.
C
      COMMON /REFF/ JOPT,IOPEN
      COMMON /NEW2/ JLINE
      CHARACTER *36 TREAD
      CHARACTER *80 LINE,JLINE(3)
C     SAVE TREAD,KOPEN
      LOGICAL YN
C
      KDUM=1
      ITIME=ITIME+1
      IF (ITIME.EQ.1.OR.KOPEN.EQ.0)GO TO 100
  120 WRITE (1,110)
  110 FORMAT (/,'DO YOU WISH TO USE THE SAME REFERENCE FILE?')
      IF (.NOT.YN(KDUM)) GO TO 100
      CLOSE (UNIT=13)
      GC TO 25
  100 WRITE (1,10)
   10 FORMAT (/,'ENTER REFERENCE FILE NAME:  (HIT <CR> TO OMIT)')
      READ (1,20) TREAD
   20 FORMAT (A36)
C     WRITE(1,9909) TREAD(1:1)
C9909 FORMAT('TREAD',A1,'IS IT HERE')
      IF (TREAD(1:1).NE.' ')GO TO 25
      IOPEN=0
      GO TO 30
   25 OPEN (UNIT=13,FILE=TREAD,STATUS='OLD')
```

```
      IOPEN=1
   30 KOPEN=IOPEN
      RETURN
      END
C
C  THIS SUBROUTINE READS INTEGER VALUES FROM THE TERMINAL AND
C  CHECKS TO SEE THAT THEY ARE ENTERED PROPERLY.
C
      SUBROUTINE QUESTB (J,L,IVAL,IMIN,IMAX,M,*)
      COMMON /REFF/ JOPT,IOPEN
      COMMON /PN/ NFLAG
      COMMON /EE/ EXIT,LIST,JFLAG
      COMMON /NEW1/ LINE
      COMMON /NEW2/ JLINE
      COMMON /NEW4/ CHAR,F
      CHARACTER *80 STRING
      CHARACTER *80 LINE,JLINE(3)
      CHARACTER *72 QUESTN
      CHARACTER *40 FMT
      CHARACTER *16 CHAR,CHAR1
      CHARACTER *4 F,F1
      CHARACTER *2 FO(16)
C     CHARACTER *1 ONOFF
      INTEGER IVAL
      LOGICAL EXIT,LIST,NONB
      DATA FO/'1 ','2 ','3 ','4 ','5 ','6 ','7 ','8 ','9 ','10','11'
     1,'12','13','14','15','16' /
      DATA QUESTN /'KEEP THE OLD VALUE? (HIT <RETURN> IF YOU DO; IF NO
     1T, REENTER THE DATA)'/
C
C         K=0 ==> CHARACTER STRING
C         K=1 ==> REAL
C         K=2 ==> INTEGER
C
      K=2
  100 IF (J.GT.0.AND.J.LT.10) I=1
      IF (J.GE.10.AND.J.LT.100) I=2
      IF (J.GE.100) I=3
      IF (NFLAG.GT.0.OR.JOPT.EQ.2) GO TO 30
      IF (J.GT.0) GO TO 10
      FMT='(/,''INPUT '',A'//FO(L)//')'
      WRITE (1,FMT) CHAR
      GO TO 300
   10 FMT='(/,''INPUT '',A'//FO(L)//',''('',I'//FO(I)//',''))'
      WRITE (1,FMT) CHAR,J
      GO TO 300
   30 IF (J.GT.0) GO TO 40
      FMT='(/,''OLD '',A'//FO(L)//',''='','//F//',/,A72)'
      IF (K.EQ.2) WRITE (1,FMT) CHAR,IVAL,QUESTN
      IF (K.NE.2) WRITE (1,FMT) CHAR,STRING,QUESTN
      GO TO 300
   40 FMT='(/,''OLD '',A'//FO(L)//',''('',I'//FO(I)//',''))='','//F//',
     1/,A72)'
      IF (K.EQ.2) WRITE (1,FMT) CHAR,J,IVAL,QUESTN
      IF (K.NE.2) WRITE (1,FMT) CHAR,J,STRING,QUESTN
C
C     READ RESPONSE
C
  300 JFLAG=0
      READ (1,105) LINE
  105 FORMAT(A80)
C
C          JFLAG=0 ---> PROPER ENTRY
C          JFLAG=1 ---> EXPLANATION IS ASKED
C          JFLAG=2 ---> A NULL ANSWER
C          JFLAG=3 ---> ANSWER OF WRONG TYPE
C          JFLAG=4 ---> SPECIAL CHARACTERS
C
      IF (LINE(1:2).NE.' ') GO TO 110
      JFLAG=2
  110 IF (LINE(1:1).EQ.'?') JFLAG=1
      CALL SPECL (M)
      IF (EXIT.OR.LIST) JFLAG=4
      IF (JFLAG.NE.0) GO TO 200
      GO TO (140,150,120), K+1
  140 STRING=LINE
      GO TO 200
  120 READ (LINE,*,ERR=130) IVAL
      GO TO 200
  150 READ (LINE,*,ERR=130) G
C
C     MAKE SURE THAT DECIMAL POINT IS PRESENT
C
      NONB=.FALSE.
      DO 155 I2=1,80
      IF (LINE(I2:I2).NE.' ') NONB=.TRUE.
      IF (NONB.AND.LINE(I2:I2).EQ.' ') GO TO 130
      IF (LINE(I2:I2).EQ.'.') GO TO 156
  155 CONTINUE
      GO TO 130
  156 STRING=LINE
      GO TO 200
C
  130 JFLAG=3
  200 IF (JFLAG.EQ.2.AND.(NFLAG.NE.0.OR.JOPT.EQ.2)) GO TO 170
      IF (JFLAG.EQ.4) RETURN
      IF (JFLAG.NE.0) RETURN 1
  170 IF (K.NE.2.OR.IMAX.LE.IMIN) RETURN
      IF (IVAL.GT.IMAX.OR.IVAL.LT.IMIN) RETURN 1
      RETURN
      END
End of file
```

Appendix 3.5 Procedure for Running PHREEQE and PHRQIN

Running PHREEQE and PHRQIN at the University of Alberta

If you have access to the IBM Amdahl 580 computer at the University of Alberta, the following files are accessible at read status:

1. FWSS:PHRQ.INPT- FORTRAN listing of PHRQIN
2. FWSS:PHRQ.INOBJ- Compiled version of PHRQIN
3. FWSS:PHRQ.MINDAT- Mineral data base
4. FWSS:PHRQ.DATBASE- Thermodynamic data base of PHREEQE
5. FWSS:PHREEQE- FORTRAN listing of PHREEQE
6. FWSS:PHRQ.OBJ- Compiled version of PHREEQE
7. FWSS:PHRQ.RUN- Source file for running PHREEQE
8. FWSS:PHRQ.INRUN- Source file for running PHRQ.INPT

You can build your own run files from the above files, but the most convenient method of running both PHREEQE and PHRQIN is to do the following:

1. Invoke PHRQ.INPT by entering:

   ```
   #SO FWSS:PHRQ.INRUN
   ```

   This sources the file FWSS:PHRQ.INRUN which contains:

   ```
   > 1.1 $EM -OUT1
   > 2   $R FWSS:PHRQ.INOBJ 11=FWSS:PHRQ.MINDAT 12=FWSS:PHRQ.DATBASE
         1=*sink* T=5
   ```

2. Answer the prompts given by PHRQ.INPT by entering values for the variables described in the PHREEQE manual. The output will be written in the temporary file -out1 (provided that you answer -out1 as the output file name when prompted by the program)

3. Once the input data have been entered with PHRQ.INPT, PHREEQE can be invoked by entering:

```
#SO FWSS:PHRQ.RUN
```

   This sources the file FWSS:PHRQ.RUN which contains:

```
>      1      $em -out2
>      2      $R FWSS:PHRQ.OBJ 5=-OUT1 6=-OUT2  10=FWSS:PHRQ.DATBASE T=5
```

   The results of the simulation will be stored in <u>temporary</u> file -out2 .

4. If you wish to save the data file and the results file for future reference, remember to rename the temporary files -out1 and -out2, respectively, with permanent names.

Note 1: PHREEQE and PHRQIN are written in FORTRAN. Both programs were compiled using a VS-extended level FORTRAN compiler.

Note 2: An error message will be given after each key word is entered during a run with PHRQ.INPT. This error message is a relic and will not interfere with the execution of the program. Ignore the message and continue with the next prompt.

Appendix 3.6 Example of a PHREEQE Simulation

Example of a PHREEQE Simulation

The objective of this simulation is to determine the amount of $BaSO_{4(s)}$ (barite) that will dissolve in five solutions generated by the irreversible reaction of varying amounts of oxygen with pyrite. The solutions initially consist of distilled water in equilibrium with pyrite, hematite and barite. Hematite equilibrium controls the total iron in solution and barite equilibrium is specified to determine the amount of $BaSO_{4(s)}$ that will dissolve in the solutions. Oxygen is reacted with the solutions in concentrations of 0.0, 0.001, 0.005, 0.01 and 0.05 mol/kg of oxygen. The simulation was conducted using the interactive preformatting program PHRQIN. A summary of the input data, a copy of the session conducted with PHRQIN and the print-out of the results of the simulation are given in the following sections.

Summary of Input Data

Input Options

IOPT(1) = 0	no print-out of thermodynamic data or coefficients of aqueous species
IOPT(2) = 1	pH is adjusted in the initial solution to obtain charge balance; pH will also vary according to the reactions
IOPT(3) = 3	a stoichiometric reaction is added in specified reaction steps
IOPT(4) = 0	temperature is held constant
IOPT(5) = 1	the pe of the reaction solution is determined by the reaction
IOPT(6) = 1	the WATEQ Debye-Huckel formula is used for all species with GFLAG = 1; the Davies formula is used for all other species
IOPT(7) = 0	the aqueous phase composition at the end of the reaction is not saved for future simulations
IOPT(8) = 0	the debugging print routine is not called
IOPT(9) = 0	no print-out of each array to be solved
NSTEPS = 5	the number of reaction steps
NCOMPS = 1	the number of constituents in a net stoichiometric reaction

SOLUTION Input

NTOTS = 0	the number of elements comprising the initial solution
PH = 7.	estimate of initial pH
PE = 4.	estimate of initial pe
TEMP = 25.	temperature of the initial solution

REACTION Input

LREAC(1) = 32	index number of the element in the reaction (32 = oxygen)
CREAC(1) = 1.	stoichiometric coefficient of the element in the reaction
THMEAN(1) = 4.	the OPV (operational valence) of the element in the reaction; the OPV is defined as the valence of any species which can change valence (can be oxidized or reduced) under naturally occurring conditions

STEPS Input

XSTEP(1) = 0.0	moles of reaction to be added to the solution in step 1
XSTEP(2) = 0.001	moles of reaction to be added to the solution in step 2
XSTEP(3) = 0.005	moles of reaction to be added to the solution in step 3
XSTEP(4) = 0.01	moles of reaction to be added to the solution in step 4
XSTEP(5) = 0.05	moles of reaction to be added to the solution in step 5

MINERALS Input

Barite, Hematite and Pyrite	mineral phases to be maintained at equilibrium with the reaction solution

INTERACTIVE SESSION WITH PHRQIN

```
[illegible]
```

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

```
[illegible]

[illegible]

[illegible] STOP' TO EXIT

[illegible]

[illegible] INDEX [illegible] OF MINERAL (TYPE 'STOP' TO EXIT)

[illegible]

[illegible] THE INDEX NUMBER OF MINERAL (TYPE 'STOP' TO EXIT)

MORE MINERALS TO BE TYPED IN FROM THE TERMINAL?
```

[illegible]

[illegible] DATA [illegible]

[illegible]

[illegible]

RESULTS OF THE SIMULATION

```
PYRITE IS OXIDIZED BY O2 - HEMATITE CONTROLS FE - BASO4 IS DISSOLVED
0130110000 5 1          0.0
SOLUTION 1
DISTILLED WATER
 0  0 0      7.00      4.00      25.0       1.00
MINERALS
BARITE     2      6.00     -9.98      6.28         0               0.0
  11   1.00       16   1.00
HEMATITE   3      6.00     -4.01     -30.8         0               0.0
 115   2.00        3   3.00        1 -6.00
PYRITE     4     0.0       -18.5      11.3         0               0.0
   1  -2.00        2  -2.00       8   1.00       42   2.00
           0     0.0       0.0       0.0           0               0.0
STEPS
 0.0       0.100E-02 0.500E-02 0.100E-01 0.500E-01
REACTION
  32    1.000   4.000
```

```
SOLUTION NUMBER 1          DISTILLED WATER


                              TOTAL MOLALITIES OF ELEMENTS
                              ----- ---------- -- --------

                         ELEMENT          MOLALITY         LOG MOLALITY

                         PURE WATER



                              ----DESCRIPTION OF SOLUTION----

                                            PH =    6.9990
                                            PE =    4.0000
                                  ACTIVITY H2O =    1.0000
                                IONIC STRENGTH =    0.0000
                                   TEMPERATURE =   25.0000
                            ELECTRICAL BALANCE =    0.0
                                          THOR =   -1.4224E-25
                               TOTAL ALKALINITY =    1.0027E-07
                                    ITERATIONS =    5


                               ----------------------
                               DISTRIBUTION OF SPECIES
                               ----------------------

  I   SPECIES     Z       MOLALITY    LOG MOLALITY    ACTIVITY    LOG ACTIVITY     GAMMA       LOG GAMMA

  1   H+         1.0   1.00268E-07     -6.9988    1.00231E-07     -6.9990    9.99628E-01    -0.0002
  2   E-        -1.0   1.00000E-04     -4.0000    1.00000E-04     -4.0000    1.00000E+00     0.0
  3   H2O        0.0   1.00000E+00     -0.0000    1.00000E+00     -0.0000    1.00000E+00     0.0
 31   OH-       -1.0   1.00268E-07     -6.9988    1.00231E-07     -6.9990    9.99628E-01    -0.0002
 33   H2 AQ      0.0   7.11214E-26    -25.1480    7.11214E-26    -25.1480    1.00000E+00     0.0000

                              ---- LOOK MIN IAP ----

                        PHASE        LOG IAP      LOG KT     LOG IAP/KT

                        O2 GAS      -42.0840     -2.9600     -39.1240
                        H2 GAS      -25.1480     -3.1500     -21.9980
```

```
STEP NUMBER  1
--------------

                    0.0       MOLES OF REACTION HAVE BEEN ADDED.


                   REACTION IS:
                              1.00 MOLES OF O2          VALENCE =    4.000


                              TOTAL MOLALITIES OF ELEMENTS
                              ----- ---------- -- --------

                         ELEMENT          MOLALITY  *       LOG MOLALITY

                         PURE WATER



                               ----PHASE BOUNDARIES----

                  PHASE      DELTA PHASE*       LOG IAP      LOG KT       LOG IAP/KT

                 BARITE      1.059405E-05       -9.9760      -9.9760       -0.0000
                 HEMATITE    2.697521E-08       -4.0080      -4.0080       -0.0000
                 PYRITE      4.160625E-09      -18.4800     -18.4800       -0.0000
* NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.


                              ---- LOOK MIN IAP ----

                      PHASE        LOG IAP      LOG KT      LOG IAP/KT

                      BARITE       -9.9760      -9.9760      -0.0000
                      HEMATITE     -4.0080      -4.0080      -0.0000
                      GOETHITE     -2.0040       0.5000      -2.5040
                      FEOH3A       -2.0040       4.8910      -6.8950
                      PYRITE      -18.4800     -18.4800      -0.0000
                      FES PPT      -9.5271      -3.9150      -5.6121
                      O2 GAS      -70.6103      -2.9600     -67.6503
                      H2 GAS      -10.8849      -3.1500      -7.7349


                             TOTAL MOLALITIES OF ELEMENTS
                             ----- ---------- -- --------

                       ELEMENT          MOLALITY           LOG MOLALITY

                       FE            5.811104E-08           -7.2357
                       BA            1.059405E-05           -4.9749
                       S             1.060237E-05           -4.9746
                    ----DESCRIPTION OF SOLUTION----

                                  PH =   7.2062
                                  PE =  -3.3388
                        ACTIVITY H2O =   1.0000
                      IONIC STRENGTH =   0.0000
                         TEMPERATURE =  25.0000
                  ELECTRICAL BALANCE =  -1.3984E-15
                                THOR =   6.3726E-05
                     TOTAL ALKALINITY =   1.6338E-07
                          ITERATIONS =  23


                        ----------------------
                        DISTRIBUTION OF SPECIES
                        ----------------------

  I   SPECIES    Z     MOLALITY    LOG MOLALITY   ACTIVITY    LOG ACTIVITY     GAMMA      LOG GAMMA

  1   H+        1.0  6.26724E-08    -7.2029    6.21970E-08    -7.2062    9.92415E-01    -0.0033
  2   E-       -1.0  2.18174E+03     3.3388    2.18174E+03     3.3388    1.00000E+00    0.0
  3   H2O       0.0  1.00000E+00    -0.0000    1.00000E+00    -0.0000    1.00000E+00    0.0
  8   FE+2      2.0  5.77218E-08    -7.2387    5.59902E-08    -7.2519    9.70002E-01    -0.0132
 11   BA+2      2.0  1.05939E-05    -4.9749    1.02761E-05    -4.9882    9.70002E-01    -0.0132
 16   SO4-2    -2.0  1.06016E-05    -4.9746    1.02842E-05    -4.9878    9.70063E-01    -0.0132
 31   OH-      -1.0  1.62756E-07    -6.7885    1.61521E-07    -6.7918    9.92415E-01    -0.0033
 33   H2 AQ     0.0  1.30359E-11   -10.8849    1.30361E-11   -10.8849    1.00001E+00    0.0000
 40   HSO4-    -1.0  6.25614E-11   -10.2037    6.20868E-11   -10.2070    9.92415E-01    -0.0033
 41   S-2      -2.0  6.62193E-16   -15.1790    6.42329E-16   -15.1922    9.70002E-01    -0.0132
 42   HS-      -1.0  3.32526E-10    -9.4782    3.30004E-10    -9.4815    9.92415E-01    -0.0033
 43   H2S       0.0  2.01506E-10    -9.6957    2.01508E-10    -9.6957    1.00001E+00    0.0000
105   FEOH+     1.0  2.86846E-10    -9.5424    2.84670E-10    -9.5457    9.92415E-01    -0.0033
106   FEOH2     0.0  3.89548E-14   -13.4094    3.89552E-14   -13.4094    1.00001E+00    0.0000
107   FEOH3-   -1.0  2.34482E-17   -16.6299    2.32703E-17   -16.6332    9.92415E-01    -0.0033
108   FESO4     0.0  1.02395E-10    -9.9897    1.02396E-10    -9.9897    1.00001E+00    0.0000
109   FE(HS)2   0.0  5.38469E-18   -17.2688    5.38474E-18   -17.2688    1.00001E+00    0.0000
110   FE(HS)3- -1.0  1.94086E-25   -24.7120    1.92614E-25   -24.7153    9.92415E-01    -0.0033
115   FE+3      3.0  2.55312E-24   -23.5929    2.38402E-24   -23.6227    9.33768E-01    -0.0298
116   FEOH+2    2.0  2.56310E-19   -18.5912    2.48622E-19   -18.6045    9.70002E-01    -0.0132
117   FEOH2+    1.0  1.33376E-15   -14.8749    1.32365E-15   -14.8782    9.92415E-01    -0.0033
118   FEOH3     0.0  2.50029E-16   -15.6020    2.50031E-16   -15.6020    1.00001E+00    0.0000
119   FEOH4-   -1.0  4.05071E-17   -16.3925    4.01998E-17   -16.3958    9.92415E-01    -0.0033
125   FESO4+    1.0  2.06436E-25   -24.6852    2.04870E-25   -24.6885    9.92415E-01    -0.0033
126   FESO42-  -1.0  6.71361E-29   -28.1730    6.66268E-29   -28.1764    9.92415E-01    -0.0033
163   BAOH+     1.0  7.30074E-12   -11.1366    7.24537E-12   -11.1399    9.92415E-01    -0.0033
200   BASO4     0.0  1.08142E-10    -9.9660    1.08143E-10    -9.9660    1.00001E+00    0.0000
```

```
STEP NUMBER  2
--------------

              1.000E-03 MOLES OF REACTION HAVE BEEN ADDED.


             REACTION IS:
                         1.00 MOLES OF O2          VALENCE =    4.000

                         TOTAL MOLALITIES OF ELEMENTS
                         ----- ---------- -- --------

                  ELEMENT            MOLALITY           LOG MOLALITY

                  PURE WATER


                         ----PHASE BOUNDARIES----

            PHASE       DELTA PHASE*        LOG IAP         LOG KT          LOG IAP/KT

           BARITE      2.798610E-07         -9.9760         -9.9760
           HEMATITE    1.493649E-04         -4.0080         -4.0080         -0.0000
           PYRITE      3.070520E-04        -18.4800        -18.4800         -0.0000
                                                                            -0.0000
* NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

                          ---- LOOK MIN IAP ----

               PHASE          LOG IAP         LOG KT         LOG IAP/KT

              BARITE          -9.9760         -9.9760         -0.0000
              HEMATITE        -4.0080         -4.0080         -0.0000
              GOETHITE        -2.0040          0.5000         -2.5040
              FEOH3A          -2.0040          4.8910         -6.8950
              PYRITE         -18.4800        -18.4800         -0.0000
              FES PPT        -10.8128         -3.9150         -6.8978
              O2 GAS         -67.1820         -2.9600        -64.2220
              H2 GAS         -12.5990         -3.1500         -9.4490


                        TOTAL MOLALITIES OF ELEMENTS
                        ----- ---------- -- --------

               ELEMENT           MOLALITY            LOG MOLALITY

               FE              6.057819E-04            -3.2177
               BA              2.798610E-07            -6.5531
               S               6.143838E-04            -3.2116
```

```
                    ----DESCRIPTION OF SOLUTION----

                                    PH =    4.8207
                                    PE =   -0.0962
                          ACTIVITY H2O =    1.0000
                        IONIC STRENGTH =    0.0023
                           TEMPERATURE =   25.0000
                    ELECTRICAL BALANCE =   -6.8792E-11
                                  THOR =    4.8979E-03
                       TOTAL ALKALINITY =    1.0836E-08
                            ITERATIONS =   17


                     ------------------------
                     DISTRIBUTION OF SPECIES
                     ------------------------

  I    SPECIES     Z       MOLALITY     LOG MOLALITY    ACTIVITY     LOG ACTIVITY     GAMMA       LOG GAMMA

   1   H+         1.0   1.59327E-05     -4.7977     1.51108E-05     -4.8207    9.48411E-01    -0.0230
   2   E-        -1.0   1.24796E+00      0.0962     1.24796E+00      0.0962    1.00000E+00     0.0
   3   H2O        0.0   9.99980E-01     -0.0000     9.99980E-01     -0.0000    1.00000E+00     0.0
   8   FE+2       2.0   5.67658E-04     -3.2459     4.59275E-04     -3.3379    8.09071E-01    -0.0920
  11   BA+2       2.0   2.79753E-07     -6.5532     2.26340E-07     -6.6452    8.09071E-01    -0.0920
  16   SO4-2     -2.0   5.75548E-04     -3.2399     4.66915E-04     -3.3308    8.11253E-01    -0.0908
  31   OH-       -1.0   7.00983E-10     -9.1543     6.64820E-10     -9.1773    9.48411E-01    -0.0230
  33   H2 AQ      0.0   2.51620E-13    -12.5993     2.51753E-13    -12.5990    1.00053E+00     0.0002
  40   HSO4-     -1.0   7.22084E-07     -6.1414     6.84832E-07     -6.1644    9.48411E-01    -0.0230
  41   S-2       -2.0   5.01403E-21    -20.2998     4.05670E-21    -20.3918    8.09071E-01    -0.0920
  42   HS-       -1.0   5.33895E-13    -12.2725     5.06351E-13    -12.2955    9.48411E-01    -0.0230
  43   H2S        0.0   7.50782E-11    -10.1245     7.51179E-11    -10.1243    1.00053E+00     0.0002
 105   FEOH+      1.0   1.01340E-08     -7.9942     9.61120E-09     -8.0172    9.48411E-01    -0.0230
 106   FEOH2      0.0   5.41059E-15    -14.2668     5.41345E-15    -14.2665    1.00053E+00     0.0002
 107   FEOH3-    -1.0   1.40343E-20    -19.8528     1.33102E-20    -19.8758    9.48411E-01    -0.0230
 108   FESO4      0.0   3.81137E-05     -4.4189     3.81339E-05     -4.4187    1.00053E+00     0.0002
 109   FE(HS)2    0.0   1.03935E-19    -18.9832     1.03990E-19    -18.9830    1.00053E+00     0.0002
 110   FE(HS)3-  -1.0   6.01798E-30    -29.2205     5.70752E-30    -29.2436    9.48411E-01    -0.0230
 115   FE+3       3.0   5.50685E-17    -16.2591     3.41879E-17    -16.4661    6.20825E-01    -0.2070
 116   FEOH+2     2.0   1.81380E-14    -13.7414     1.46749E-14    -13.8334    8.09071E-01    -0.0920
 117   FEOH2+     1.0   3.39069E-13    -12.4697     3.21576E-13    -12.4927    9.48411E-01    -0.0230
 118   FEOH3      0.0   2.49891E-16    -15.6022     2.50023E-16    -15.6020    1.00053E+00     0.0002
 119   FEOH4-    -1.0   1.74457E-19    -18.7583     1.65457E-19    -18.7813    9.48411E-01    -0.0230
 120   FE2OH2+4   4.0   1.35274E-26    -25.8688     5.79641E-27    -26.2368    4.28495E-01    -0.3681
 125   FESO4+     1.0   1.40642E-16    -15.8519     1.33386E-16    -15.8749    9.48411E-01    -0.0230
 126   FESO42-   -1.0   2.07660E-18    -17.6826     1.96947E-18    -17.7057    9.48411E-01    -0.0230
 163   BAOH+      1.0   6.92578E-16    -15.1595     6.56849E-16    -15.1825    9.48411E-01    -0.0230
 200   BASO4      0.0   1.08086E-10     -9.9662     1.08143E-10     -9.9660    1.00053E+00     0.0002
```

```
STEP NUMBER  3
--------------

                    5.000E-03 MOLES OF REACTION HAVE BEEN ADDED.


                   REACTION IS:
                               1.00 MOLES OF 02         VALENCE =    4.000


                               TOTAL MOLALITIES OF ELEMENTS
                               ----- ---------- -- --------

                        ELEMENT            MOLALITY          LOG MOLALITY

                        PURE WATER



                                ----PHASE BOUNDARIES----

                 PHASE      DELTA PHASE*       LOG IAP        LOG KT        LOG IAP/KT

                BARITE      9.444243E-08       -9.9760       -9.9760          0.0000
                HEMATITE    7.569710E-04       -4.0080       -4.0080          0.0000
                PYRITE      1.536710E-03      -18.4800      -18.4800          0.0000
* NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.


                                 ---- LOOK MIN IAP ----

                     PHASE         LOG IAP        LOG KT       LOG IAP/KT

                    BARITE         -9.9760       -9.9760         0.0000
                    HEMATITE       -4.0080       -4.0080         0.0000
                    GOETHITE       -2.0040        0.5000        -2.5040
                    FEOH3A         -2.0041        4.8910        -6.8951
                    PYRITE        -18.4800      -18.4800         0.0000
                    FES PPT       -11.0721       -3.9150        -7.1571
                    02 GAS        -66.4905       -2.9600       -63.5305
                    H2 GAS        -12.9448       -3.1500        -9.7948


                              TOTAL MOLALITIES OF ELEMENTS
                              ----- ---------- -- --------

                      ELEMENT          MOLALITY           LOG MOLALITY

                      FE            3.050652E-03           -2.5156
                      BA            9.444243E-08           -7.0248
                      S             3.073514E-03           -2.5124
```

```
----DESCRIPTION OF SOLUTION----

                PH =   4.4532
                PE =   0.4442
      ACTIVITY H2O =   0.9999
    IONIC STRENGTH =   0.0102
       TEMPERATURE =  25.0000
ELECTRICAL BALANCE =   9.4135E-11
              THOR =   2.4542E-02
  TOTAL ALKALINITY =   1.7018E-08
        ITERATIONS =  23


        ------------------------
        DISTRIBUTION OF SPECIES
        ------------------------

  I   SPECIES     Z      MOLALITY    LOG MOLALITY     ACTIVITY    LOG ACTIVITY     GAMMA       LOG GAMMA

  1   H+         1.0   3.90964E-05     -4.4079     3.52186E-05     -4.4532    9.00814E-01    -0.0454
  2   E-        -1.0   3.59605E-01     -0.4442     3.59605E-01     -0.4442    1.00000E+00     0.0
  3   H2O        0.0   9.99904E-01     -0.0000     9.99904E-01     -0.0000    1.00000E+00     0.0
  8   FE+2       2.0   2.54485E-03     -2.5943     1.67573E-03     -2.7758    6.58478E-01    -0.1815
 11   BA+2       2.0   9.43345E-08     -7.0253     6.21172E-08     -7.2068    6.58478E-01    -0.1815
 16   SO4-2     -2.0   2.56127E-03     -2.5915     1.70133E-03     -2.7692    6.64252E-01    -0.1777
 31   OH-       -1.0   3.16629E-10     -9.4994     2.85224E-10     -9.5448    9.00814E-01    -0.0454
 33   H2 AQ      0.0   1.13285E-13    -12.9458     1.13552E-13    -12.9448    1.00236E+00     0.0010
 40   HSO4-     -1.0   6.45631E-06     -5.1900     5.81594E-06     -5.2354    9.00814E-01    -0.0454
 41   S-2       -2.0   9.29379E-22    -21.0318     6.11975E-22    -21.2133    6.58478E-01    -0.1815
 42   HS-       -1.0   1.97634E-13    -12.7041     1.78032E-13    -12.7495    9.00814E-01    -0.0454
 43   H2S        0.0   6.14116E-11    -10.2117     6.15565E-11    -10.2107    1.00236E+00     0.0010
105   FEOH+      1.0   1.67014E-08     -7.7772     1.50449E-08     -7.8226    9.00814E-01    -0.0454
106   FEOH2      0.0   3.62698E-15    -14.4405     3.63554E-15    -14.4394    1.00236E+00     0.0010
107   FEOH3-    -1.0   4.25723E-21    -20.3709     3.83497E-21    -20.4162    9.00814E-01    -0.0454
108   FESO4      0.0   5.05787E-04     -3.2960     5.06981E-04     -3.2950    1.00236E+00     0.0010
109   FE(HS)2    0.0   4.67939E-20    -19.3298     4.69044E-20    -19.3288    1.00236E+00     0.0010
110   FE(HS)3-  -1.0   1.00480E-30    -29.9979     9.05138E-31    -30.0433    9.00814E-01    -0.0454
115   FE+3       3.0   1.10831E-15    -14.9553     4.32891E-16    -15.3636    3.90587E-01    -0.4083
116   FEOH+2     2.0   1.21066E-13    -12.9170     7.97194E-14    -13.0984    6.58478E-01    -0.1815
117   FEOH2+     1.0   8.31990E-13    -12.0799     7.49469E-13    -12.1252    9.00814E-01    -0.0454
118   FEOH3      0.0   2.49407E-16    -15.6031     2.49995E-16    -15.6021    1.00236E+00     0.0010
119   FEOH4-    -1.0   7.87922E-20    -19.1035     7.09771E-20    -19.1489    9.00814E-01    -0.0454
120   FE2OH2+4   4.0   9.09848E-25    -24.0410     1.71054E-25    -24.7669    1.88003E-01    -0.7258
125   FESO4+     1.0   6.83174E-15    -14.1655     6.15413E-15    -14.2108    9.00814E-01    -0.0454
126   FESO42-   -1.0   3.67552E-16    -15.4347     3.31097E-16    -15.4800    9.00814E-01    -0.0454
163   BAOH+      1.0   8.58545E-17    -16.0662     7.73390E-17    -16.1116    9.00814E-01    -0.0454
200   BASO4      0.0   1.07889E-10     -9.9670     1.08143E-10     -9.9660    1.00236E+00     0.0010
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STEP NUMBER  4
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                    1.000E-02 MOLES OF REACTION HAVE BEEN ADDED.


                    REACTION IS:
                                    1.00 MOLES OF O2         VALENCE =   4.000


                                        TOTAL MOLALITIES OF ELEMENTS
                                        ----- ---------- -- --------

                              ELEMENT            MOLALITY          LOG MOLALITY

                              PURE WATER


                                          ----PHASE BOUNDARIES----

                         PHASE      DELTA PHASE*       LOG IAP       LOG KT        LOG IAP/KT

                         BARITE     6.507745E-08       -9.9760      -9.9760          0.0000
                         HEMATITE   1.519340E-03       -4.0080      -4.0080          0.0000
                         PYRITE     3.074192E-03      -18.4800     -18.4800         -0.0000
 * NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.

                                          ---- LOOK MIN IAP ----

                           PHASE        LOG IAP       LOG KT       LOG IAP/KT

                           BARITE        -9.9760      -9.9760        0.0000
                           HEMATITE      -4.0080      -4.0080        0.0000
                           GOETHITE      -2.0040       0.5000       -2.5040
                           FEOH3A        -2.0041       4.8910       -6.8951
                           PYRITE       -18.4800     -18.4800       -0.0000
                           FES PPT      -11.1719      -3.9150       -7.2569
                           O2 GAS       -66.2242      -2.9600      -63.2642
                           H2 GAS       -13.0780      -3.1500       -9.9280


                                       TOTAL MOLALITIES OF ELEMENTS
                                       ----- ---------- -- --------

                            ELEMENT          MOLALITY          LOG MOLALITY

                            FE             6.112872E-03          -2.2138
                            BA             6.507745E-08          -7.1866
                            S              6.148449E-03          -2.2112
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                              ----DESCRIPTION OF SOLUTION----

                                          PH =    4.3120
                                          PE =    0.6520
                              ACTIVITY H2O =    0.9998
                            IONIC STRENGTH =    0.0191
                               TEMPERATURE =   25.0000
                        ELECTRICAL BALANCE =    9.6293E-10
                                      THOR =    4.9116E-02
                          TOTAL ALKALINITY =    2.0706E-08
                                ITERATIONS =   26


                              -----------------------
                              DISTRIBUTION OF SPECIES
                              -----------------------

  I   SPECIES     Z      MOLALITY    LOG MOLALITY    ACTIVITY    LOG ACTIVITY      GAMMA       LOG GAMMA

   1  H+         1.0   5.58528E-05     -4.2530     4.87523E-05     -4.3120     8.72871E-01     -0.0591
   2  E-        -1.0   2.22856E-01     -0.6520     2.22856E-01     -0.6520     1.00000E+00      0.0
   3  H2O        0.0   9.99814E-01     -0.0001     9.99814E-01     -0.0001     1.00000E+00      0.0
   8  FE+2       2.0   4.74603E-03     -2.3237     2.75505E-03     -2.5599     5.80497E-01     -0.2362
  11  BA+2       2.0   6.49698E-08     -7.1873     3.77147E-08     -7.4235     5.80497E-01     -0.2362
  16  SO4-2     -2.0   4.76643E-03     -2.3218     2.80214E-03     -2.5525     5.87890E-01     -0.2307
  31  OH-       -1.0   2.36034E-10     -9.6270     2.06027E-10     -9.6861     8.72871E-01     -0.0591
  33  H2 AQ      0.0   8.32019E-14    -13.0799     8.35679E-14    -13.0780     1.00440E+00      0.0019
  40  HSO4-     -1.0   1.51913E-05     -4.8184     1.32600E-05     -4.8775     8.72871E-01     -0.0591
  41  S-2       -2.0   5.09529E-22    -21.2928     2.95780E-22    -21.5290     5.80497E-01     -0.2362
  42  HS-       -1.0   1.36460E-13    -12.8650     1.19112E-13    -12.9240     8.72871E-01     -0.0591
  43  H2S        0.0   5.67609E-11    -10.2460     5.70105E-11    -10.2440     1.00440E+00      0.0019
 105  FEOH+      1.0   2.04694E-08     -7.6889     1.78671E-08     -7.7479     8.72871E-01     -0.0591
 106  FEOH2      0.0   3.10503E-15    -14.5079     3.11868E-15    -14.5060     1.00440E+00      0.0019
 107  FEOH3-    -1.0   2.72241E-21    -20.5650     2.37631E-21    -20.6241     8.72871E-01     -0.0591
 108  FESO4      0.0   1.36683E-03     -2.8643     1.37284E-03     -2.8624     1.00440E+00      0.0019
 109  FE(HS)2    0.0   3.43677E-20    -19.4638     3.45188E-20    -19.4619     1.00440E+00      0.0019
 115  FE+3       3.0   3.90442E-15    -14.4084     1.14843E-15    -14.9399     2.94137E-01     -0.5315
 116  FEOH+2     2.0   2.63166E-13    -12.5798     1.52767E-13    -12.8160     5.80497E-01     -0.2362
 117  FEOH2+     1.0   1.18852E-12    -11.9250     1.03743E-12    -11.9840     8.72871E-01     -0.0591
 118  FEOH3      0.0   2.48867E-16    -15.6040     2.49962E-16    -15.6021     1.00440E+00      0.0019
 119  FEOH4-    -1.0   5.87284E-20    -19.2312     5.12623E-20    -19.2902     8.72871E-01     -0.0591
 120  FE2OH2+4   4.0   5.53179E-24    -23.2571     6.28152E-25 .  -24.2019     1.13553E-01     -0.9448
 125  FESO4+     1.0   3.08067E-14    -13.5114     2.68903E-14    -13.5704     8.72871E-01     -0.0591
 126  FESO42-   -1.0   2.72982E-15    -14.5639     2.38278E-15    -14.6229     8.72871E-01     -0.0591
 163  BAOH+      1.0   3.88585E-17    -16.4105     3.39184E-17    -16.4696     8.72871E-01     -0.0591
 200  BASO4      0.0   1.07670E-10     -9.9679     1.08144E-10     -9.9660     1.00440E+00      0.0019
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STEP NUMBER  5
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                        5.000E-02 MOLES OF REACTION HAVE BEEN ADDED.


                       REACTION IS:
                                 1.00 MOLES OF 02         VALENCE =    4.000


                                         TOTAL MOLALITIES OF ELEMENTS
                                         ----- ---------- -- --------

                           ELEMENT           MOLALITY          LOG MOLALITY

                           PURE WATER


                                           ----PHASE BOUNDARIES----

                       PHASE      DELTA PHASE*        LOG IAP       LOG KT       LOG IAP/KT

                      BARITE      3.356381E-08        -9.9760      -9.9760         0.0000
                      HEMATITE    7.634302E-03        -4.0080      -4.0080         0.0000
                      PYRITE      1.537633E-02       -18.4800     -18.4800         0.0000

         * NEGATIVE DELTA PHASE INDICATES PRECIPITATION AND POSITIVE DELTA PHASE INDICATES DISSOLUTION.


                                            ---- LOOK MIN IAP ----

                           PHASE         LOG IAP        LOG KT      LOG IAP/KT

                          BARITE         -9.9760       -9.9760        0.0000
                          HEMATITE       -4.0080       -4.0080        0.0000
                          GOETHITE       -2.0042        0.5000       -2.5042
                          FEOH3A         -2.0046        4.8910       -6.8956
                          PYRITE        -18.4800      -18.4800        0.0000
                          FES PPT       -11.3813       -3.9150       -7.4663
                          O2 GAS        -65.6658       -2.9600      -62.7058
                          H2 GAS        -13.3575       -3.1500      -10.2075


                                         TOTAL MOLALITIES OF ELEMENTS
                                         ----- ---------- -- --------

                           ELEMENT           MOLALITY          LOG MOLALITY

                           FE             3.064493E-02          -1.5136
                           BA             3.356381E-08          -7.4741
                           S              3.075269E-02          -1.5121
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POOR
QUALITY
ORIGINAL